Chemical Science

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Journal:	*Chemical Science*
Manuscript ID:	SC-EDG-09-2014-002872.R1
Article Type:	Edge Article
Date Submitted by the Author:	20-Oct-2014

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Chemical Science

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EDGE ARTICLE

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The transition-metal-free controlled polymerization for poly(*p*-aryleneethynylene)s is developed. The polymerization of 1-pentafluorophenyl-4-[(trimethylsilyl)ethynyl]benzene with a catalytic amount of fluoride anion proceeds in a chain-growth-like manner to afford the polymers with controlled molecular weight and low polydispersity index. The mechanism involves a pentacoordinated fluorosilicate as a key intermediate. The anionic "living" nature of this process is applied to block copolymerization and also surface-terminated polymerization.

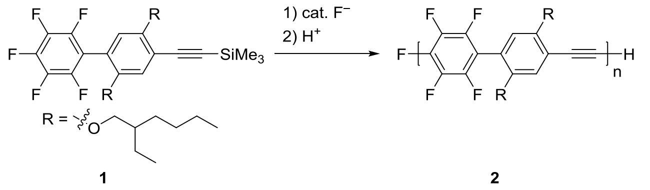
Introduction

Among the most extensively studied families of molecular optoelectronic materials, such as organic field-effect transistors (FETs) and organic electroluminescent (EL) devices, poly(*p*-aryleneethynylene)s (PAEs) are one of the most important types of materials.[1] The polymers are commonly prepared by polycondensations using Sonogashira- or Stille-type cross couplings[2] or by an alkyne metathesis.[3] In all cases, however, the molecular weight (MW) and polydispersity index (PDI) of the polymers are not controlled because the polycondensations proceed by a step-growth mechanism. In contrast to these conventional step-growth polycondensations, chain-growth polymerizations have been demonstrated recently, but requires transition-metal catalysts.[4] There remains a need to produce additional syntheses of well-defined polymers with control of the MW, polydispersity, modification of the end group, and also block copolymerization, which could offer new architectures and materials.[5]

Here, we describe a transition-metal-free controlled polymerization for PAEs. The polymerization proceeds in a chain-growth-like manner to afford the polymers with controlled MW and low PDI. This could be an alternative synthetic method for well-controlled PAEs.

Results and discussion

We designed 1-pentafluorophenyl-4-[(trimethylsilyl)ethynyl]benzene **1** as a monomer and examined the polymerization with a catalytic amount of fluoride anion (Scheme 1). This is because fluoride anion catalyzed silylacetylene activation to react with a number of electrophiles[6,7] and also the regioselective S$_N$Ar reaction of perfluoroaryl groups with nucleophiles[8,9] are well studied. Very recently, we demonstrated the transition-metal-free polymerization of 2-perfluoroaryl-5-trimethylsilylthiophenes promoted by fluoride anion to afford polymers with controlled MW and low PDI.[10] In contrast, the reported polycondensation of hexafluorobenzene and 1,4-bis[(trimethylsilyl)ethynyl]benzene was not controlled.[11] Recently, Bielawski et al. reported a controlled Pd catalyst transfer polycondensation for poly(*p*-phenyleneethynylene).[12]



Scheme 1 Polymerization of **1**.

A catalytic amount of fluoride anion smoothly promoted the polymerization of **1**. Table 1 summarizes the polymerization results. For example, the reaction of **1** with 5 mol % tetrabutylammonium fluoride (TBAF)[13] as a fluoride anion source in tetrahydrofuran (THF) at room temperature for 2 h led to poly(*p*-tetrafluorophenylene–phenylene–ethynylene) **2** with a number-averaged MW (M_n) of 4400 and a PDI of 1.31 in 81% isolated yield (entry 2). The MWs measured by size-exclusion

Table 1 Polymerization of **1** Catalyzed by Fluoride Anion [a]

Entry	F^- (mol %)	reaction conditions	yield (%)	M_n[b,c]	PDI[b,c]
1	Bu_4NF (TBAF) (10)	THF, rt, 2 h	34	3950 (3600)	1.26 (1.24)
2	(5)	THF, rt, 2 h	81	4400 (4500)	1.31 (1.31)
3	(2)	THF, rt, 2 h	52	7400 (8900)	1.68 (1.68)
4	(1)	THF, rt, 2 h	82	11500 (14500)	2.11 (1.57)
5	(5)	THF, rt, 2 h[d]	48	7600	1.72
6	Me_4NF (5)	THF, rt, 2 h	71	4500	4.15
7	KF (5) / 18-C-6 (10)	THF, 80 °C, 20 h	1	1400	1.08
8	CsF (5) / 18-C-6 (10)	toluene, 80 °C, 20 h	75	13700	3.88
9	KF (5) / cryptand[2.2.2] (10)	THF, rt, 2 h	0	-	-
10	$Bu_4N^+[Ph_3SiF_2]^-$ (5)	THF, rt, 2 h	27	2500	1.48

[a] All reactions were run with [**1**] = 0.3 mmol in 5 mL solvent. [b] The number-average MW (M_n) and PDI were determined by SEC using polystyrene standards. [c] The figures in parentheses are the weight-averaged MW (M_w) and PDI determined by SEC–MALS. [d] A THF solution of **1** was added to a TBAF solution.

chromatography (SEC)–multi-angle light scattering (MALS) were almost the same as those measured by SEC. When the polymerization of **1** was examined with varying mol % of TBAF to the monomer, the MW of the polymer linearly increased with increasing monomer to TBAF ratio (entries 1–4), while the PDIs were relatively low (≤2). Addition of **1** to a solution of TBAF also gave the polymer (entry 5). However, tetramethylammonium fluoride was not a good initiator because some remained undissolved in THF (entry 6). Potassium fluoride and cesium fluoride in the presence of 18-crown-6 or cryptand[2.2.2] did not give a good result (entries 7–9). Tetrabutylammonium difluorotriphenylsilicate was not effective for the polymerization of **1** (entry 10).

The obtained polymer has a structure with high regioregularity, as demonstrated by ^1H, ^{13}C, and ^{19}F NMR analyses (Fig. S1 in the ESI). The ^1H NMR spectrum of **2** showed major signals around 0.8, 1.4, and 4.0 ppm from the side chain on the phenylene units, along with a small signal at 3.7 ppm arising from the ethynyl group at the polymer end. In the ^{19}F NMR spectrum of the polymer, two strong signals and three weak signals, which are assigned to the 1,4-tetrafluorophenylene units in the main chain and the pentafluorophenyl group at the polymer end, respectively, were found. Thus, the NMR spectra are consistent with a high regioregularity for the polymer main chain, indicating that the polymerization process itself must be highly regioselective. In addition, because the polymer ends are designated as the pentafluorophenyl and the ethynyl groups, the integral ratio of the peaks from the side chain on the main chain and the end group in the ^1H and ^{19}F NMR spectra provided a M_n of *ca*. 5000, in reasonable agreement with the MW estimated by SEC (Table 1, entry 2). Further, matrix-assisted laser desorption ionization time-of-flight (MALDI–TOF) mass spectra also indicate that the polymer has the pentafluorophenyl and the ethynyl groups at the ends (Fig. S2 in the ESI).

The controlled MW and the relatively low PDIs found in Table 1 indicate that the polymerization proceeds in a chain-growth-like manner under these conditions. To prove further this feature, we monitored the polymerization of **1** with 2.5 mol % TBAF as a function of monomer conversion. Fig. 1 shows the M_n and PDI as a function of monomer conversion. The polymerization of **1** was fast, where the conversion of **1** was up to 50% in a few minutes (Table S1 and Fig. S3 in the ESI). As shown in Fig. 1, the linear relationship between M_n and monomer conversion and the relatively low PDI confirm the chain-growth-like process.

Scheme 2 shows a possible polymerization mechanism. In the initial step of the reaction, a fluoride anion attacks the trimethylsilyl group of **1** to form a pentacoordinate silicate. The silicate is quite reactive and could regioselectively attack the 4-position of the pentafluorophenyl group of **1** to reproduce a fluoride anion. The fluoride anion would transfer intramolecularly to the trimethylsilylethynyl group at the polymer end, where there may be an anion–π interaction that produces an associated pair.[14] Then, the fluoride anion catalyzes the polymerization to give polymer **2**. In the polymerization, the reactivity of the trimethylsilyl group and/or the silicate at the polymer end is changed by replacing the 4-position of the pentafluorophenyl group of **1**. Watson et al. discussed the change in the reactivity by substitution in the polymerization of 1,4-bis[(trimethylsilyl)ethynyl]benzene and hexafluorobenzene with fluoride anions.[11] A further description of the polymerization mechanism requires further studies.

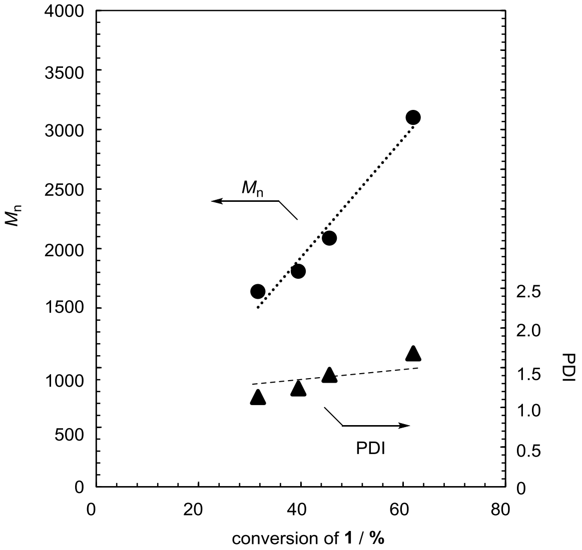
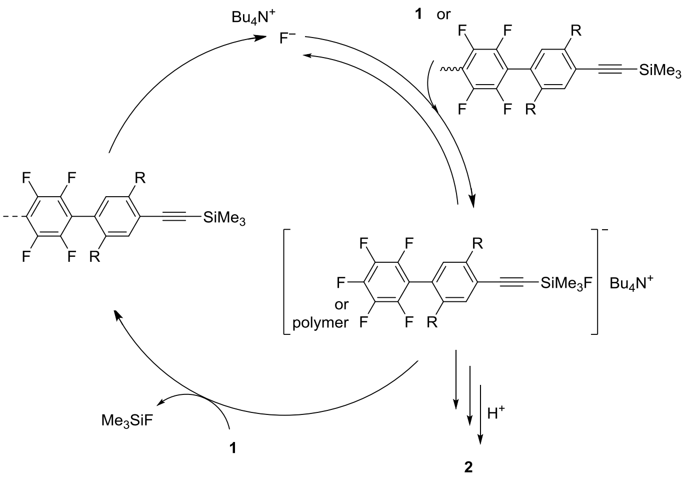
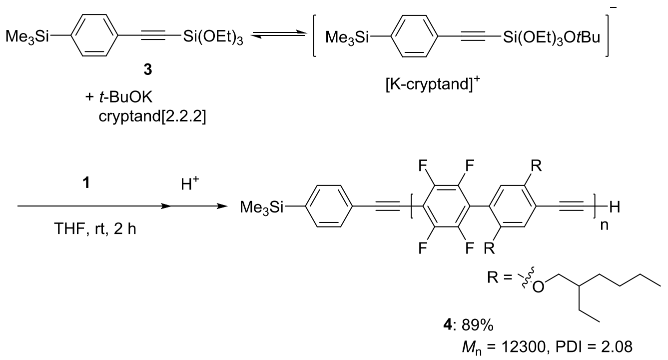


Fig. 1 M_n and PDI of polymer **2** formed as a function of monomer conversion in the polymerization of **1** with 2.5 mol % TBAF.



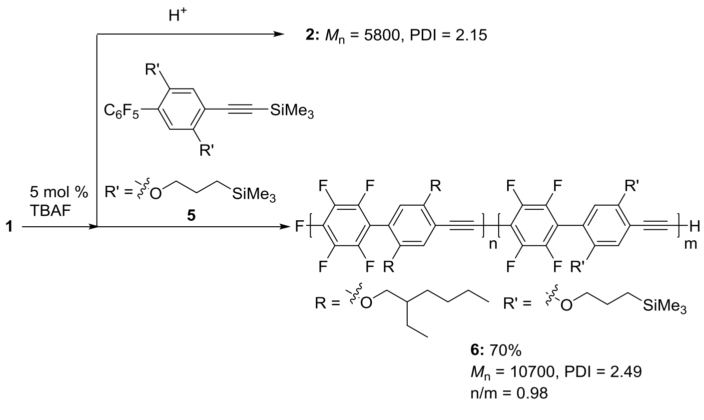
Scheme 2 Possible polymerization mechanism of **1**.

According to the polymerization mechanism, all of the propagating polymer chains contain the reactive pentacoordinate silicate at a chain terminus. Indeed, a pentacoordinated alkynylsilicate, which is prepared in situ by the reaction of 1-(4-trimethylsilyl)phenyl-2-(triethoxysilyl)acetylene **3** and potassium *t*-butoxide,[15] initiated the polymerization of **1** efficiently in the presence of cryptand[2.2.2] to give polymer **4** with a M_n of 12300 and a PDI of 2.08 in 89% yield (Scheme 3).[16] The ^{1}H NMR spectra of **4** showed peaks at around 0.3 and 3.4 ppm arising from the trimethylsilyl and ethynyl groups at the polymer ends, respectively, where the observed integral ratio is in good agreement with the calculated value (calcd for $–Si\underline{Me_3}/–C{\equiv}C\underline{H}$ 9.0, found 8.8) within the experimental errors (Fig. S4 in the ESI).[17]



Scheme 3 Polymerization of **1** with a pentacoordinated alkynylsilicate prepared by the reaction of **3** and potassium *t*-butoxide.

Next, we demonstrated the anionic "living" character of this polymerization end to the synthesis of a well-defined block copolymer (Scheme 4). After polymerization of **1** with a catalytic amount of TBAF, a part of the mixture was studied to analyze the MW of the first block, and then a solution of **5** was added to the reaction mixture to give block copolymer **6**.[18] As shown in Fig. 2, the SEC curve of the polymer obtained at the end of the reaction shifted toward higher MW than that of the first polymerization. The first/second block ratio (*n*/*m*) of **6** was found to be 0.98 by ^{1}H NMR analysis (Fig. S6 in the ESI).



Scheme 4 Synthesis of block copolymer **6**.

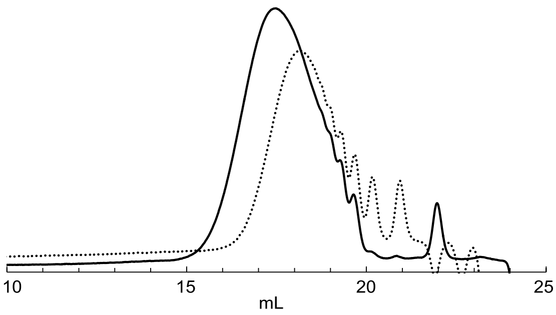
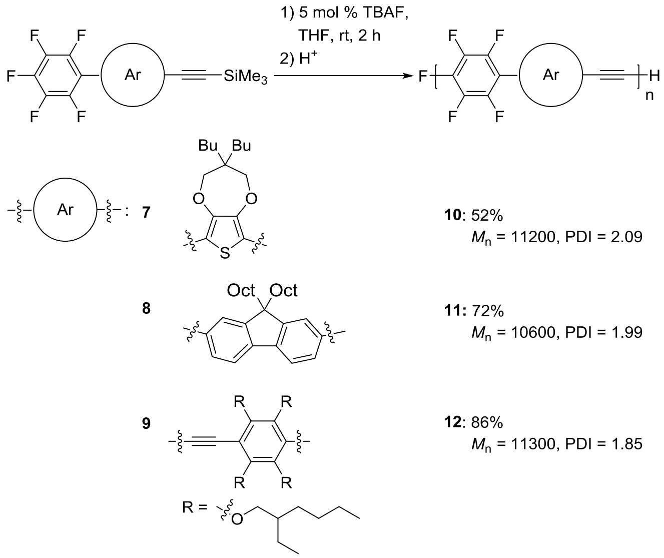


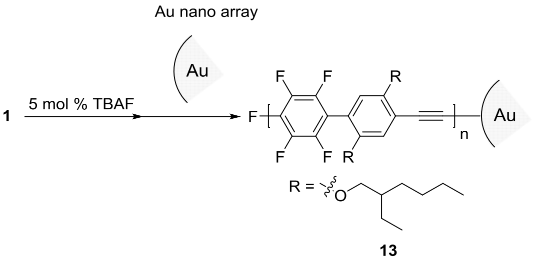
Fig. 2 SEC curves (RI) obtained by the first polymerization of **1** (polymer **2**, dotted line) and sequential addition of **5** (polymer **6**, solid line) after the first polymerization of **1**.

We also extended our method to polymerization of a variety of aromatic monomers, **7**–**9**, with trimethylsilylethynyl and pentafluorophenyl groups in the molecule (Scheme 5). The reaction of 2-pentafluorophenyl-5-[(trimethylsilyl)ethynyl]thiophene **7** with 5 mol% TBAF gave polymer **10** with a M_n of 11200 and a PDI of 2.09 in a moderate yield. Fluorene-incorporated **8** was polymerized by addition of 5 mol% TBAF to give polymer **11** with a M_n of 10600 and a PDI of 1.99 in a good yield. A phenyleneethynylene monomer **9** was also polymerized to afford polymer **12** with a M_n of 11300 and a PDI of 1.85. The structures of these polymers were highly ordered, as demonstrated by NMR analyses (Figs S7–9 in the ESI), indicating that the polymerizations also proceed with high regioselectivity.



Scheme 5. Polymerization of **7**–**9**.

Next, we turned our attention to exploring the surface-terminated polymerization of **1**. Au surfaces and nanometer-sized particles represent an ideal substrate for this study because of their well-established chemistry and a feature that could be exploited for molecular device applications.[19] The surface-terminated polymerization was accomplished by the addition of a surface-enhanced Raman scattering (SERS)-active Au nanoparticle (ϕ 15 nm) array [20] to a polymerization mixture of **1** (Scheme 6). After standing for 1 h, the plate was washed with THF and then subjected to the Raman spectroscopy. The SEC analysis of the polymerization mixture showed that the resulting polymer has a M_n of 4700 and a PDI of 1.79. The $\nu_{C\equiv C}$ stretching region in the SERS spectra is particularly informative. The Raman spectrum of **2** showed a signal around ~2200 cm^{-1} from the ethynyl groups in the polymer main chain (Fig. 3). On the other hand, in the Raman spectrum of **13**, a broad and downshifted signal also appeared at 2050 cm^{-1}. The red-shift of ~150 cm^{-1} indicates a strong interaction with the Au substrate, which is in agreement with previous reports.[21] Thus, the ethynyl group of the polymer end is attached to the gold substrate via covalent Au–C≡C bonds. Although this is a preliminarily demonstration, but represents a possible step for molecular device applications. Further details will be reported.



Scheme 6 Surface termination for the polymerization of **1** with Au nanoparticle array.

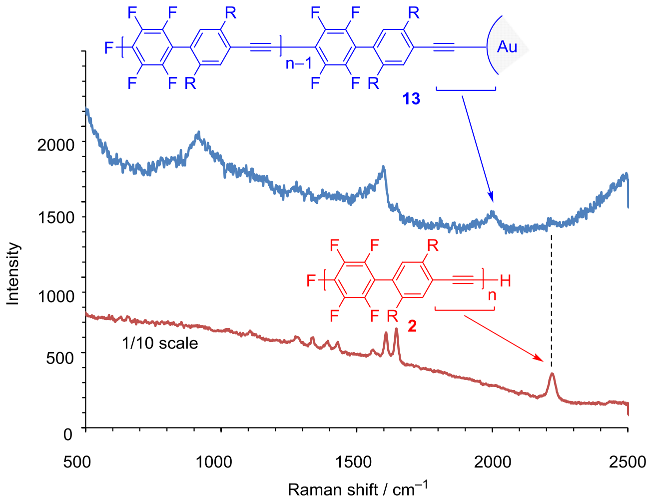


Fig. 3 Raman spectra of **2** (film, red) and **13** (blue).

Conclusions

We have developed a transition-metal-free controlled synthesis of PAEs promoted by fluoride anion. The polymerization proceeds in an anionic chain-growth-like manner to afford PAEs with controlled MW and relatively low PDI. The polymerization end is active to afford a block copolymer. We also demonstrated the synthesis of the surface-terminated PAE on a Au nanoparticle array. We expect that this concept can be extended to prepare other well-controlled conjugated polymers with new opportunities in optoelectronic and other applications. Further study along this line is currently in progress.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterization of new compounds and polymers. See DOI: 10.1039/b000000x/

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16 When pentacoordinated trimethyl silicates, which were prepared in situ by the reaction of 1-phenyl-2-(trimethylsilyl)acetylene with potassium *t*-butoxide or TBAF as a Lewis base, were used as an initiator, the polymerizations were not initiated effectively at the initiator (the introduction ratio of the initiator unit ≈ 10–50%, see Fig S5 in the ESI). This is because the reaction of trimethylsilyl groups of the 1-phenyl-2-(trimethylsilyl)acetylene and **1** with the Lewis bases is in equilibrium and the initiation did not occur preferentially at the initiator units.

17 In the ^{19}F NMR, however, three weak signals, which are assignable to the pentafluorophenyl group at the polymer end, besides two strong signals of the 1,4-tetrafluorophenylene units in the main chain, were found. This indicates that not all of the polymerizations were initiated at the initiator, but the introduction ratio of the initiator unit is ≈ 80% (see in the ESI).

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A catalytic amount of fluoride anion promoted the polymerization of 1-pentafluorophenyl-4-[(trimethylsilyl)ethynyl]benzene, providing a high-molecular-weight polymer in a chain-growth-like manner.