Macromolecules

Article

Cite This: *Macromolecules* 2020, 53, 240−248

pubs.acs.org/Macromolecules

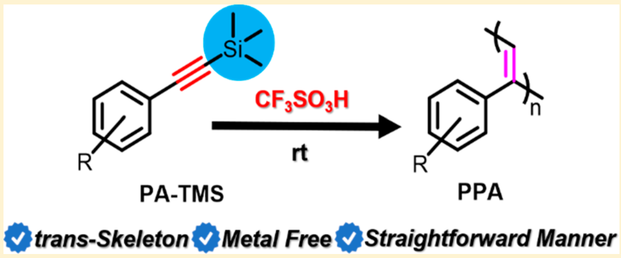
Silicon Promoted Cationic Polymerization of Phenylacetylenes

Bing Zhao, Hailong Ma, Chonggang Wang, Zhikun Shang, Yun Ding,* and Aiguo Hu*

Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

Supporting Information

ABSTRACT: Poly(phenylacetylene)s (PPAs) are widely applied in a variety of research fields due to their good electrical and optical properties. Transition-metal-catalyzed polymerizations are generally performed for the synthesis of PPAs, while the residual metal catalysts might be problematic. In this work, we present a silicon promoted cationic polymerization of phenylacetylenes (PAs) by introducing a labile and electron-donating silyl group at the alkynyl termini of PA monomers. The polymerizations were performed in the presence of trifluoromethanesulfonic acid to rapidly produce the PPA products with good yields. The structures of the PPAs were characterized by NMR, IR, MALDI-TOF MS, UV−vis, and fluorescence spectroscopies, showing that the PPAs consist of conjugated skeletons with high contents of *trans*-configurations. GPC analysis showed a relatively narrow molecular weight distribution, and the molecular weight reached up to 4.7 kDa. A possible reaction scheme was proposed through further analysis on the structures of three kinds of oligomeric species. As the silyl groups are generally inherited from Sonogashira coupling reactions during the synthesis of PAs, this work presents a straightforward and metal-free method for the synthesis of PPAs.



INTRODUCTION

The conductivity of doped polyacetylenes (PAs) was first discovered by Heeger, MacDiarmid, and Shirakawa,[1−3] opening a new era of conducting polymers. In the past decades, PAs have been investigated intensively due to their promising electrical conductivity,[4−6] photoconductivity,[7,8] light emission,[9] liquid crystallinity,[10,11] gas permeability,[12] and their ability to be fabricated into useful materials for various applications.[6,13−18] On the other hand, the general application of PAs is limited due to their low solubility and stability.[19] To this end, with the introduction of aryl groups, poly(phenylacetylene)s (PPAs) with good solubility in common solvents and high stability in air have received increasing research interests.[20]

PPAs are obtained mainly through metathesis or coordination/insertion pathway.[21] Transition metal complexes[22] are used as the catalysts for these polymerizations. Early transition metal catalysts include Ziegler−Natta[23] catalysts and group 6 metal carbene complexes of molybdenum[24] and tungsten,[25,26] while for late-transition-metal catalysts, the best studied are rhodium and palladium complexes. Since 1969, Kern's first report on the use of a Rh catalyst, $(Ph_3P)_3RhCl$, to polymerize PA,[27] the late-transition-metal catalysts have drawn particular attention thanks to their high activity, stability, and the relatively wide monomer scope.[28]

The main disadvantages of metal-based catalysts are related to their high cost and complicated synthesis.[29] Moreover, the residual metal complexes in polymeric products might be problematic especially for plastic electronic applications. Therefore, developing a metal-free polymerization method for the synthesis of PPAs is of essential importance. Superacid-catalyzed reactions have drawn our attention as several kinds of polymers were synthesized from this kind of polymerization at room temperature with high yields and selectivity, and with such a method, materials were fabricated with good physical and thermal properties.[30−33] Meanwhile, the triple bonds of PAs are prone to be attacked by the superacid. By utilization of organic sulfonic acids, cationic alkyne benzannulations generally proceeded in high to quantitative yield,[34,35] and treating PAs with organic sulfonic acids either directly or in the presence of additives has been confirmed as a straightforward way to synthesize vinyl sulfonate esters.[36,37] Polymerization of PAs catalyzed with a superacid, however, has not been explored due to the relatively low chain propagating potency of terminal PAs in the presence of superacids, which resulted in a mixture of low-molecular-weight oligomers.

Herein, we report a silicon promoted cationic polymerization method to produce PPAs in high yield and high *trans*-contents under mild conditions. We proved that the chain extending potency of PAs was greatly enhanced upon the introduction of a labile and electron-donating silyl group at the alkynyl termini to give polymers with high molecular weight (MW). A series of PPAs with different substituents at the phenyl ring were synthesized in a straightforward way, and their structures were characterized with NMR, FT-IR, UV−vis, GPC, and fluorescence spectroscopies as well as matrix-assisted

Received: October 16, 2019
Revised: December 2, 2019
Published: December 24, 2019

DOI: 10.1021/acs.macromol.9b02191
Macromolecules 2020, 53, 240−248

laser desorption ionization/time-of-flight mass spectrometry (MALDI-TOF MS). Two dimers and one trimer with different chain-ending structures were trapped, and their molecular structures were fully characterized. Based on these findings, a plausible polymerization mechanism was proposed for this new cationic polymerization of PAs.

■ EXPERIMENTAL SECTION

Materials. Dichloromethane, 1,2-dichloroethane, tetrahydrofuran (THF), and triethylamine (Et_3N) are of general commercial grade. They were dried over calcium hydride (CaH_2) and distilled before use. Phenylethynyltrimethylsilane (**PA1-TMS**) and phenylacetylene (**PA1-H**) were obtained from Energy Chemical (Shanghai, China) and used as received; the substituted PAs were synthesized according to a general literature procedure.[38] Other chemical reagents were of commercial grade and used without further treatment. All Sonogashira reactions (for the preparation of monomers) and polymerizations were performed with dry Schlenk techniques under nitrogen.

Characterizations. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded in chloroform-*d* ($CDCl_3$) or dichloromethane-d_2 (CD_2Cl_2) on a Bruker Avance III 400 NMR spectrometer. ^{13}C NMR (101 or 151 MHz) spectra were recorded in chloroform-*d* ($CDCl_3$) or dichloromethane-d_2 (CD_2Cl_2) on a Bruker Avance III 400 or 600 NMR spectrometer. Chemical shifts were referenced to Me_4Si. FT-IR analysis was performed using KBr pellets on a Nicolet Magna 5700 FT-IR spectrometer. UV−vis absorption spectra were recorded in dichloromethane on a PerkinElmer Lambda 950 at room temperature. Fluorescence spectra were recorded in dichloromethane on a PerkinElmer LS-55 (excited at 365 nm). Mass spectra (MS) of the monomers were recorded on a Micromass LCTTM mass spectrometer by using the electrospray ionization (ESI) method. MALDI-TOF MS of polymers was performed on a mass spectrometer 4800 plus a MALDI-TOF/TOF MS analyzer (AB Sciex, USA) equipped with a Nd:YAG laser emitting at 355 nm and operating at an accelerating voltage of 20 kV in reflection mode. A 4000 series Explorer and a DATA Explorer (AB Sciex, USA) were used for data acquisition and processing. The extraction delay time was set to 450 ns. All mass spectra were collected by averaging the signals of 500 individual laser shots. Dried-droplet samples were prepared by spotting a 1 μL aliquot of a mixture of 1 mL of matrix (1,8,9-anthracenetriol, 10 mg/mL in THF), 0.1 mL of polymer (5 mg/mL in THF), and 0.1 mL of salt (silver trifluoroacetate, 5 mg/mL in methanol) on the target plate. The number-averaged molecular weight (M_n) and the polydispersity index (PDI) of the polymers were determined by a twice-detector gel permeation chromatograph (Malvern Panalytical, Viscotek) equipped with a refractive index detector (RI2RALLS), and a multiangle static laser light scattering (RI2MALLS) detector was used, with a normal flow rate of 1 mL/min at 40 °C, in THF. The differential scanning calorimetry (DSC) experiments were performed on a SPA409PC thermal analyzer. For the fluorescence quantum yield (FQY) measurement in solution, quinine sulfate (350 nm, 0.54, 0.1 M H_2SO_4) was used as the standard.

$$\phi_x = \phi_{st}(I_x/I_{st})(\eta 2x/\eta 2st)(A_{st}/A_x)$$

where ϕ is the FQY, I is the measured integrated emission intensity, η is the refractive index of the solvent, and A is the optical density. The subscript "*st*" refers to standard with known FQY and "*x*" for the sample.[39]

General Procedure for the Synthesis of Substituted PAs. (4-Methylphenylethynyl)trimethylsilane (**PA3-TMS**): CuI (114.2 mg, 0.6 mmol) and $Pd(PPh_3)Cl_2$ (200 mg, 0.3 mmol) were added to a 100 mL dried flask. Then degassed THF (30 mL), Et_3N (15 mL), 4-iodotoluene (1.3 g, 6 mmol), and trimethylsilylacetylene (TMSA, 1.77 g, 18 mmol) were successively added under a nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 24 h. The dark brown solution was washed with saturated NH_4Cl solution and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified through column chromatography (silica, petroleum ether) to yield a yellow liquid (0.91 g, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.7, 132.0, 129.1, 120.2, 105.5, 93.4, 21.3, 0.2.

Other PAs were prepared and purified by following a similar procedure as described for PA3-TMS, and their characterization data are listed in the Supporting Information.

General Procedure for Silicon Promoted Cationic Polymerization of PAs. A solution of **PA1-TMS** (1.0 g, 5.7 mmol) in 1,2-dichloroethane (5 mL) was cooled to −78 °C, and then CF_3SO_3H (2.56 g, 17.1 mmol, 3 equiv) was added under a nitrogen atmosphere. The mixture quickly turned dark and was allowed to warm to room temperature and further stirred for 4 h before the addition of wet methanol (or saturated $NaHCO_3$) to quench the polymerization and partitioned with saturated aqueous NaCl solution and dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The product was obtained by precipitation into a large amount of methanol or hexane followed by collection with centrifugation to give dark brown powders (0.34 g, 52%).

Trapping and Identification of the Oligomeric Products. A solution of **PA2-TMS** (((2,6-difluorophenyl)ethynyl)trimethylsilane)(1.0 g, 4.8 mmol) in 1,2-dichloroethane (5 mL) was cooled to −78 °C, and then CF_3SO_3H (2.15 g, 14.4 mmol) was added under a nitrogen atmosphere. After stirring at −78 °C for 5 min, the dark brown solution was quenched by injecting large excess of saturated $NaHCO_3$ solution. The mixture was washed with saturated NaCl solution and extracted with dichloromethane, and then the organic phase was dried over anhydrous $MgSO_4$. This mixture contains unreacted monomer, two different kinds of dimers (**D1** and **D2**), one trimer (**T1**), and other inseparable oligomeric products. After careful column chromatography separation (silica, petroleum ether:ethyl acetate = 10:1), we obtained and identified these three small molecular compounds.

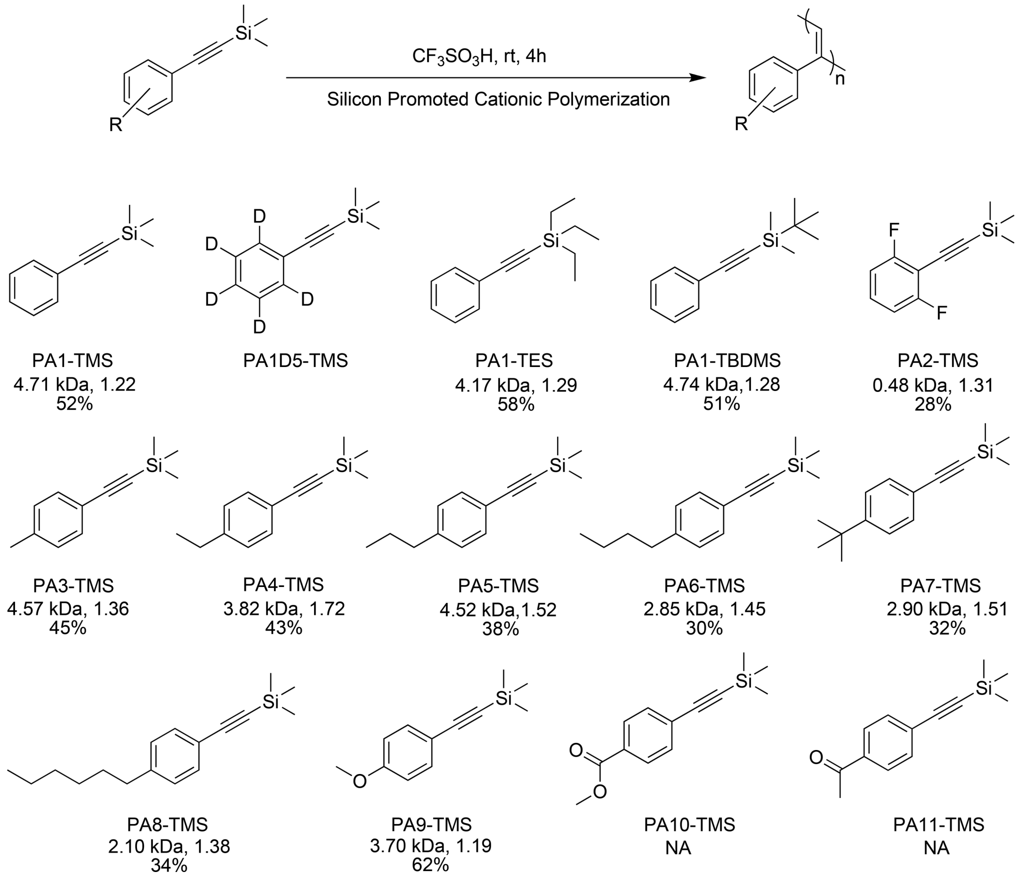
2,2′-(But-3-en-1-yne-1,3-diyl)bis(1,3-difluorobenzene) (**D1**, 25 mg, 4%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (m, 2H), 6.90−6.76 (m, 4H), 6.09 (s, 1H), 5.76 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3, 163.2, 160.8, 160.7, 160.3, 160.2, 157.8, 157.7, 129.5, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 117.5, 114.8, 110.7, 110.6, 110.5, 110.5, 110.3, 110.19, 110.1, 110.0, 101.1, 96.7, 96.7, 96.6, 74.6. HRMS (ESI): m/z calcd for $C_{16}H_8F_4$ (276.0562); found: 276.0563.

Trifluoromethyl (*E*)-1,3-Bis(2,6-difluorophenyl)buta-1,3-diene-1-sulfonate (**D2**, 23 mg, 3%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.18−7.10 (m, 1H), 7.00−6.91 (m, 1H), 6.93 (s, 1H), 6.62 (t, J = 8.0 Hz, 2H), 6.57 (t, J = 8.0 Hz, 2H), 5.92 (s, 1H), 5.56 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 160.3, 160.0, 159.9, 157.8, 157.7, 157.5, 157.5, 135.5, 132.0, 131.9, 131.8, 128.8, 128.7, 128.6, 128.4, 127.7, 122.2, 119.0, 115.8, 113.5, 113.3, 113.1, 112.6, 110.1, 109.9, 109.7, 109.6, 108.2, 108.0, 107.8. HRMS (ESI): m/z calcd for $C_{17}H_9F_7O_3S$ (426.0161); found: 426.0158.

Trifluoromethyl (1*E*,3*E*)-1,3,5-Tris(2,6-difluorophenyl)hexa-1,3,5-triene-1-sulfonate (**T1**, 35 mg, 5%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.06 (s, 1H), 7.01 (s, 1H), 6.95 (s, 1H), 6.88−6.83 (m, 1H), 6.64−6.58 (m, 1H), 6.53 (t, J = 8.1 Hz, 2H), 6.49−6.44 (m, 2H), 6.14 (t, J = 8.0 Hz, 2H), 5.88 (s, 1H), 5.47 (s, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 161.3, 161.2, 160.9, 160.8, 160.8, 160.7, 159.6, 159.6, 159.2, 159.1, 142.1, 136.2, 134.0, 133.6, 133.5, 133.4, 131.5, 131.2, 131.1, 131.0, 129.9, 129.8, 129.7, 122.6, 120.0, 117.8, 116.2, 116.1, 115.9, 111.6, 111.5, 111.4, 111.3, 111.2, 111.1, 111.0, 110. 9, 110.8, 110.62, 110.6, 110.5, 109.7, 109.5, 109.4. HRMS (ESI): m/z calcd for $C_{25}H_{13}F_9O_3S$ (564.0442); found: 564.0437.

Trapping and Identification of the Side Products. A solution of **PA2-TMS** (1.0 g, 4.8 mmol) in 1,2-dichloroethane (5 mL) was cooled to −78 °C, and then CF_3SO_3H (2.15 g, 14.4 mmol) was added under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and further stirred for 2 h before the addition of Et_3N (14.55 g, 144 mmol). Then, a solution of α-phenylethanol (1.22

Scheme 1. Schematic Illustration of Silicon Promoted Cationic Polymerization and the Structures of All the PAs Used in This Work[a]



[a] The numbers below each structure are the M_n, PDI, and yield (after workup) of each polymer synthesized from the corresponding monomer.

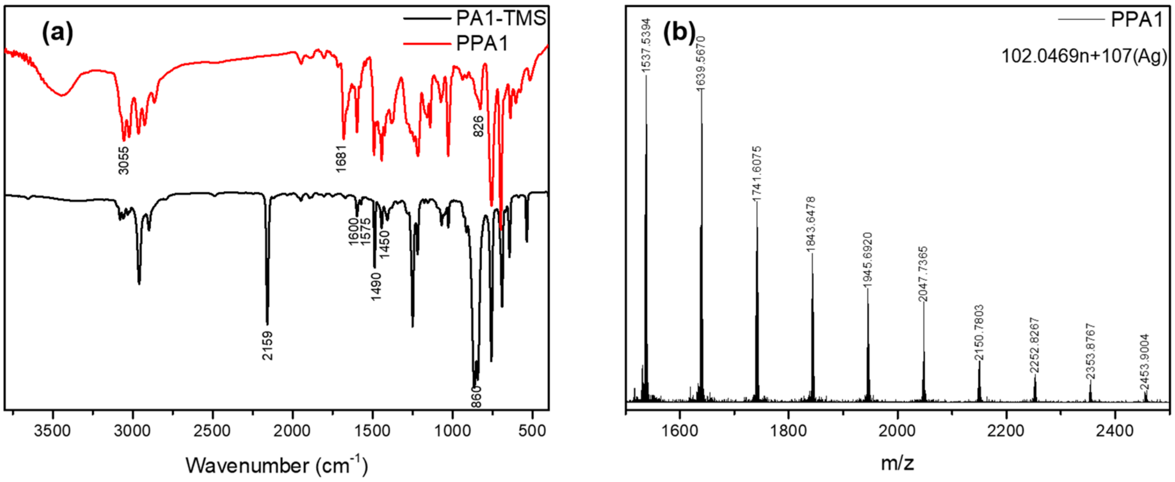


Figure 1. (a) Comparison of FT-IR spectra of **PA1-TMS** and **PPA1**. (b) MALDI-TOF MS of **PPA1**.

g, 10 mmol) in 1,2-dichloroethane (10 mL) was added to trap the side product trimethylsilyl trifluoromethanesulfonate.[40] After further stirring for 2 h, the solution was quenched by saturated $NaHCO_3$ solution, and the mixture was washed with saturated NaCl solution and extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and concentrated to be purified through column chromatography (silica, petroleum ether:ethyl acetate = 100:1) to give the product which was identified as (α-methylbenzyl)-(trimethylsilyl) ether (**M1**, 1.12 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 4.92 (q, J = 6.4 Hz, 1H), 1.50 (d, J = 6.4 Hz, 3H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 128.1, 126.8, 125.2, 70.6, 26.9, 0.0. HRMS (ESI): m/z calcd for $C_{11}H_{18}OSi$ (194.1127); found: 194.1128.

■ RESULTS AND DISCUSSION

Silyl groups at the alkynyl termini of PAs are inherited from the synthesis of these compounds through Sonogashira coupling reactions in which trialkylsilylacetylenes are typically used as acetylene equivalents. Therefore, all the silyl-group-capped PA monomers (except **PA1-TMS** which was from commercial source) used in this work were simply synthesized from trialkylsilylacetylene and corresponding phenyl halide derivatives according to the literature procedure with minor modifications.[41]

Directly treating terminal phenylacetylenes with a superacid, CF_3SO_3H, resulted in rapid formation of a mixture of vinyl triflate and polymeric products. This reaction has been thoroughly studied with the addition of various kinds of additives to limit the formation of polymeric product and give vinyl triflate in high yield.[36,37,42] Indeed, when the reaction mixture of phenylacetylene (**PA1-H**) and CF_3SO_3H was precipitated with methanol, a polymeric product with low MW was obtained in low yield (Table S1), implying a low chain propagating potency. By installing an electron-donating[35] trimethylsilyl (TMS) group at the alkynyl termini, we found that the cationic polymerization of **PA1-TMS** proceeded rapidly to give the polymeric **PA1** (**PPA1**) in moderate to high yield. The polymer exhibits high solubility in common organic solvents like dichloromethane, THF, and ethyl acetate. A direct comparison of FT-IR spectra of monomer (**PA1-TMS**) and polymer (**PPA1**) is shown in Figure 1a. The peaks at 1600, 1575, 1490, and 1450 cm^{-1} are characteristic bands attributed to the phenyl ring, which can be found in both monomer and polymer. A stretching vibration band of the double bond at 1681 cm^{-1} appears after polymerization, indicating the existence of carbonyl group in the polymer,[43] which will be discussed below. It is noteworthy that both the stretching vibrations at 2159 cm^{-1} of a triple bond and the band at 860 cm^{-1} of a C−Si bond in monomer disappear after the polymerization, which represents the complete reaction of monomers.

NMR analysis on the **PPA1** shows that no peak corresponding to the TMS group presents in both ^1H and ^{13}C NMR spectra (Figure S2), suggesting that the labile TMS group has been completely removed from the polymeric chains. The broad peaks at about 6.5−7.8 ppm (^1H NMR) and 110−160 ppm (^{13}C NMR) indicate the formation of conjugated polymer with a *trans*-structure.[44−46] To eliminate the influence of phenyl protons on ^1H NMR analysis, we synthesized deuterated **PA1-TMS** (**PA1D5-TMS**) and performed the cationic polymerization under the same condition. ^1H NMR analysis (Figure S3) on the polymeric product also showed a broad peak at 6.5−7.8 ppm, attributing entirely to the vinyl protons and corroborating the *trans*-structure of the polymer backbone.[44−46] Meanwhile, two weak singlet peaks at 5.96 and 5.40 ppm are found in these ^1H NMR spectra, which are assigned to the methylene group. The presence of the methylene group at one end of polymer chains is a strong evidence that the initiation of polymerization occurs through H^+ attacking at the alkynyl carbon adjacent to the TMS group. The other hydrogen atom of the methylene group is installed during the hydrolysis of the TMS group[47] either in situ or at the quenching step. The number-average MW (M_n) of the **PPA1** was estimated to be around 4.7 kDa through GPC analysis. The structure of the **PPA1** was further analyzed by MALDI-TOF MS (Figure 1b). From the dominant series of signals, an equal interval consistent with the calculated m/z value of **PA1** (102.0469) is observed. Moreover, the molecular weight of each peak is integral multiple of that of **PA1**, suggesting that the polymerization is terminated through losing a proton given the fact that the polymerization is initiated by addition of a proton as discussed above.

Physical properties of **PPA1** synthesized from **PA1-H** and **PA1-TMS** were compared to demonstrate the superiority of this silicon promoted cationic polymerization method. DSC experiments showed higher melting points (T_m) and melting enthalpies (ΔH_m) of **PPA1** synthesized from **PA1-TMS** (T_m,182.16 vs 177.58 °C, and ΔH_m, 28.48 vs 25.40 J/g), reflecting a higher MW and lower content of defects of the obtained **PPA1**.[48] The UV−vis and fluorescence spectra of **PPA1** obtained from these two methods are similar to each other. However, the fluorescence quantum yield (FQY) of **PPA1** synthesized from **PA1-TMS** is higher (0.18 vs 0.10) (Figure S4), implying a higher degree of π-conjugation.

To figure out the origin of the reactivity difference between **PA1-H** and **PA1-TMS** in cationic polymerization, two parameters related to the reactivity of these two molecules, i.e., electrostatic potential (ESP) and average local ionization energy (ALIE), were obtained by computational calculations. The monomers are optimized with B3LYP/6-31G(d,p) including Grimme's D3 dispersion correction[49] using Gaussian 09 software,[50] and the optimized structures subjected to further electronic analysis in Multiwfn software[51] are shown in Figure S1. Both ESP and ALIE are calculated at the electronic density surface of 0.001 au, and the values averaged over the surface close to each atom of interest are listed in Table 1.

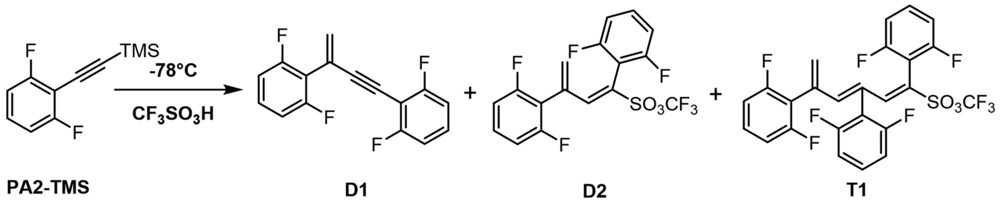
Table 1. Calculated Average ESP and ALIE of Alkynyl Carbon Atom Adjacent to Phenyl Ring (C1) or the Substituent (C2) in Two Monomers

		ESP (eV)	ALIE (eV)
PA1-TMS	C1	−15.13	9.34
	C2	−15.71	8.63
PA1-H	C1	−13.78	9.58
	C2	−13.91	8.83

Both ESP and ALIE show lower values at the alkynyl carbon atom adjacent to the hydrogen or silyl substituent (C2), which suggests lower electronegativity and in return higher reactivity when attached by electrophile.[52,53] Thus, the C2 positions in both **PA1-H** and **PA1-TMS** are susceptible to the electrophilic attack by H^+ of CF_3SO_3H to initiate the polymerization and then by the resulting carbenium ion in polymer chain propagation. Comparing both ESP and ALIE values in C2 positions of **PA1-H** and **PA1-TMS**, it is clear that **PA1-TMS** has lower values in both cases, indicating higher reactivity in the presence of silyl substituent, which is consistent with experimental findings. In addition, the hyperconjugative contribution of the β-silyl group can stabilize the developing a carbocation center which leads to a much quicker formation of positive charge.[54−56] Altogether, after the introduction of a silyl group, both the initiation and propagation steps of polymerization are greatly accelerated, resulting in polymeric product in high MW and high yield.

To obtain a deeper insight into the structure of PPAs synthesized from this method, we attempted to separate out and characterize the oligomeric species, which however turned out to be very difficult as the polymerization of **PA1-TMS** was extremely fast. To this end, a less reactive monomer (**PA2-TMS**) was synthesized by installing two electron-withdrawing fluorine atoms at two ortho-positions of the phenyl ring. It should be noted that when the polymerization of **PA2-TMS**

Scheme 2. CF_3SO_3H-Induced Reaction of PA2-TMS



was conducted for a prolonged time, a polymeric product (**PPA2**) with NMR and MALDI-TOF MS spectra similar to those of **PPA1** was obtained, guaranteeing the representativeness of this monomer. The oligomer-trapping experiment was conducted at −78 °C, and the reaction was quenched 5 min after the addition of CF_3SO_3H (Scheme 2). In the reaction mixture, three small molecular species including two dimers (**D1**, **D2**) and one trimer (**T1**) were separated, and their structures were confirmed by HR-MS and NMR analysis as shown in Figure 2. The calculated molecular weights of oligomers **D1** (276.0562), **D2** (426.0161), and **T1** (564.0442) fit well with the peaks in MS spectra at *m*/*z* 276.0563, 426.0158, and 564.0437, respectively. In the ^1H NMR spectrum, **D1** features one methylene group and one internal triple bond, suggesting that proton losing is a possible pathway for the termination of the polymerization. **D2** and **T1** are similar to each other with one methylene group at one end and one triflate group at the other end which is confirmed by the characteristic quadruplets of trifluoromethyl groups (J = 319 Hz) at 118 ppm[57] in ^{13}C NMR spectra. The sharp singlet peaks around 7.0 ppm are attributed to protons on the *trans* double bonds,[46] which is a strong evidence of *trans*-configuration of PA backbones. The presence of two singlet peaks at 5.5−6.0 of the methylene group in the polymer and all oligomeric species further confirmed that the polymerization was initiated by the H^+ attacking at the alkynyl atom adjacent to the silyl group. The fluorescence emission spectra of **PPA2** and **T1** (Figure S5) show a bathochromic shift of the maximum emission wavelength (λ_{max}) of polymer over oligomer (438 nm vs 426 nm), corroborating a higher π-conjugated degree in polymeric product.

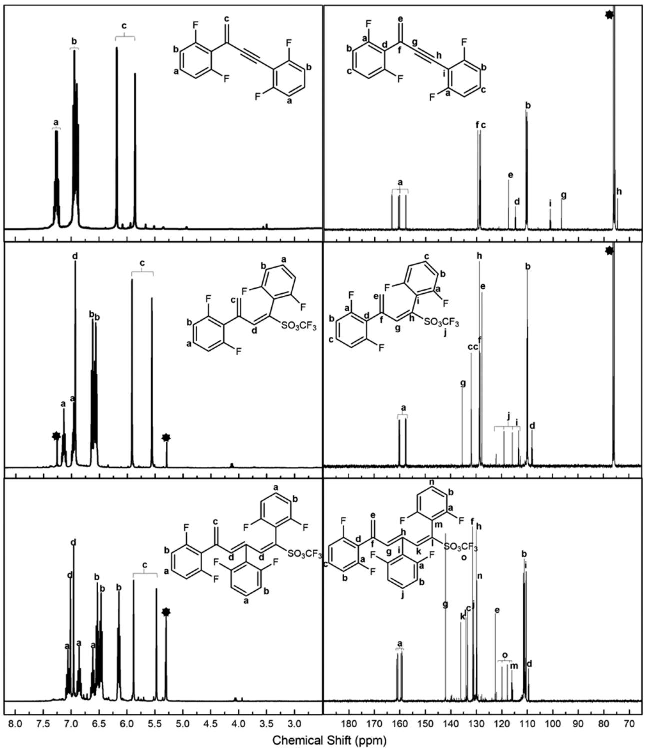


Figure 2. ^1H and ^{13}C NMR spectra of **D1**, **D2**, and **T1**. Spectra of **D1** and **D2** were recorded in $CDCl_3$, and spectra of **T1** were recorded in CD_2Cl_2. The asterisks show solvent residues.

As evidenced above, the silyl group is absent in either oligomeric species or polymeric product, suggesting that this labile group has been completely cleaved from polymer chain. To determine at which stage the TMS group was removed, we performed another quenching experiment with addition of D_2O. As shown in Figure 3, there emerge several new peaks in the MALDI-TOF spectrum of **PPA1**, corresponding to the introduction of deuterium atoms onto polymer chain at the quenching step. However, the peaks related to nondeuterated polymer chains are still strong, implying that part of the TMS groups has been cleaved before the quenching step; i.e., the cleavage of TMS is achieved by consuming some CF_3SO_3H followed by the formation of the side product TMSOTf. TMSOTf is a hygroscopic compound which cannot be purified through column chromatography; therefore, α-phenylethanol was added to the reaction mixture to trap the TMSOTf formed during the polymerization.[40] The corresponding product (**M1**) was successively separated out, and the structure was confirmed through NMR analysis. Altogether, we can conclude that during polymerization the silyl groups mainly remain on the backbone of PAs and facilitate the chain propagating process to give a high-molecular-weight product. After workup with the addition of protonic species, the silyl groups are completely scissored from the backbone to give a polymeric product free of the silicon component.

To explore the generality of this polymerization, another 11 silyl-capped PAs were synthesized with varied substituent groups either at the silyl part or the phenyl ring (Scheme 1). Most of these molecules quickly disappeared when they were treated with CF_3SO_3H. The substituents on silyl groups showed a negligible effect on the polymerization as the electronic features of TMS, TES, and TBDMS groups are similar to each other. All the alkyl-substituted PAs reacted smoothly to give the corresponding polymers in moderate to high yields. The number-average molecular weights (M_n), polydispersion index (PDI), and yields of these polymers are listed in Scheme 1. When a methoxy group was present at the phenyl ring, the MW of the obtained polymer was rather low. When an ester or a ketone group was installed on the phenyl ring, the PAs were exclusively converted to the corresponding vinyl triflate with a trace amount of dimeric product, implying rather sluggish chain propagation in these cases. We also investigated the effect of the reaction temperature and time on the polymerization. The yields and molecular weight increased

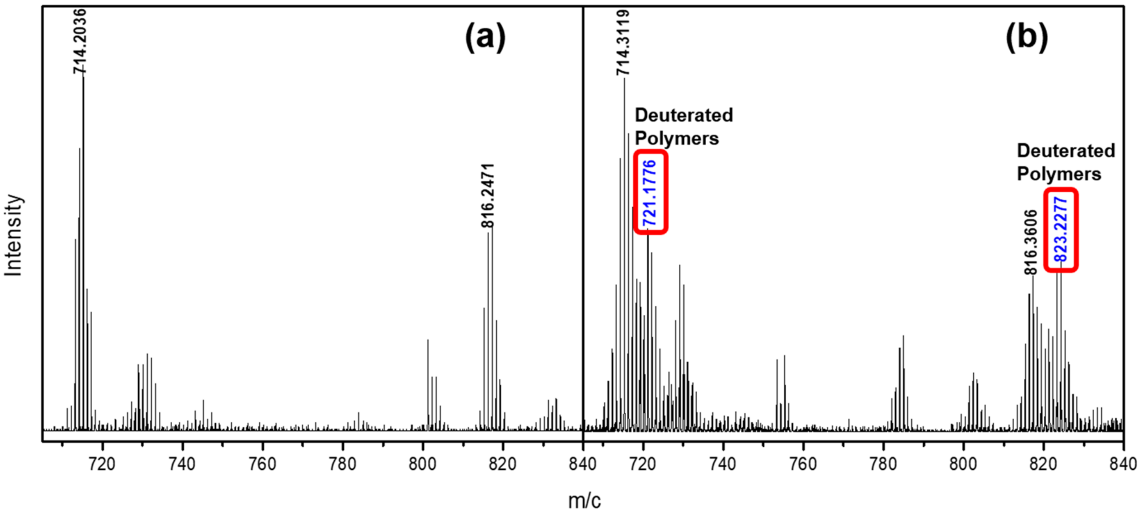
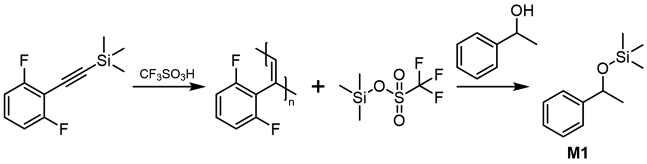


Figure 3. MALDI-TOF mass spectra of **PPA1** quenched with (a) H_2O and (b) D_2O.

Scheme 3. Reaction Scheme of TMSOTf Trapping Experiment



as the temperature and time of the reaction increase (Table S1). The maximum yield is 71% for polymerization performed for 36 h at 50 °C, but the PDI is broader than those obtained at lower temperatures and shorter times. Eventually, for polymerization at room temperature, the obtained polymer shows a good yield (54%) and molecular weight (4.7 kDa) in an easy and simple manner.

The spectroscopic characterization data of all the polymers are provided in the Supporting Information. In the ^1H NMR spectra, all the polymers showed broad peaks at about 6.5−7.8 ppm, attributed to the phenyl ring and the *trans* conjugated skeleton.[46] For the alkyl-substituted PAs, signals at 0.5−3.0 ppm are assigned to the alkyl protons. After polymerization, peaks at 80−95 ppm in the ^{13}C NMR disappeared, indicating that the triple bonds completely reacted. A series of signals with an equal interval consistent with the calculated m/z value of a monomer unit are found in all MALDI-TOF mass spectra, which is a strong evidence for the successful synthesis of structural regulated polymers. For all the polymers, the m/z values of major peak sets in MALDI-TOF exhibit integral multiple of molecular weight of the corresponding monomer unit, indicating that the major pathway of termination step is intramolecular abstraction of proton to give polymer with chain-end structure similar to **D1**. Meanwhile, minor peak sets were found in most of the MS spectra, which have a m/z value difference of 18 compared to the main peaks, relating to the hydrolysis of the triflate[47] terminal groups (similar to those in **D2** and **T1**). After this process, carbonyl groups would be formed at the chain end, which is corroborated by the presence of a carbonyl vibration band in the FT-IR spectra as mentioned above (Figure 1a). The UV−vis spectra (Figure 4a) of these polymers show strong absorption tailing to 500 nm, indicating the formation of long conjugated backbones. In fluorescence spectra (Figure 4b), the maximum emission wavelengths (λ_{max}) of polymers are between 424 and 445 nm. In addition, polymers with alkyl substituents show a clear blue-shift of λ_{max}

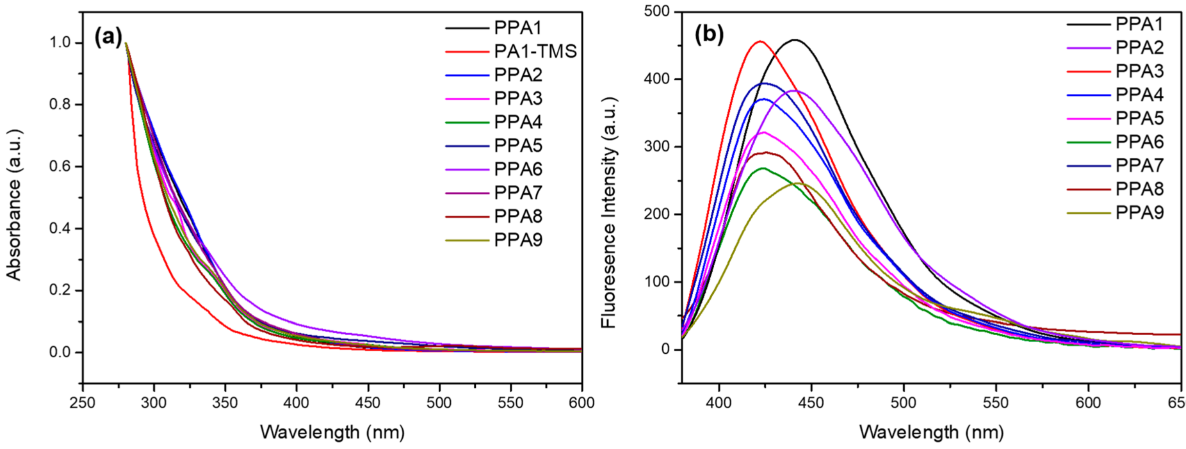


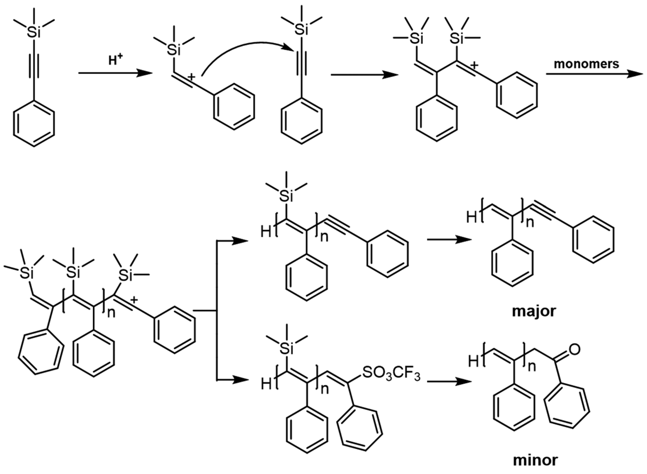
Figure 4. (a) UV−vis spectra of **PPAs** and **PA1-TMS** in dichloromethane solution ($c = 10^{-3}$ mg/mL) at room temperature. (b) Emission spectra of polymers obtained in dichloromethane solution ($c = 10^{-3}$ mg/mL). Excitation wavelength: 365 nm.

DOI: 10.1021/acs.macromol.9b02191
Macromolecules 2020, 53, 240−248

due to the steric hindrance of the long or branched alkyl chains.

Take all the above information into consideration, a possible reaction scheme is proposed, which is shown in Scheme 4. At the initiation step, the carbon atom of triple bond adjacent to the silyl group in the monomer was attacked by the H^+ of CF_3SO_3H to form a carbenium ion. The newly generated vinyl cation would then attack the next monomer in the same way to extend the main chain. The presence of a silyl group not only enhances the reactivity of these species but also guarantees a high content of the *trans*-structure through the space repulsive effect to the phenyl ring. Finally, the chain extension is terminated through two different pathways: intramolecular abstraction of a proton to form a triple bond or capped by a triflate group, which will eventually convert into a carbonyl group as a result of the hydrolysis during the workup process. All the silyl groups are eliminated during polymerization by excess CF_3SO_3H or cleaved by protonic species after the polymerization is finished.

Scheme 4. A Plausible Mechanism of Silicon Promoted Cationic Polymerization of PA



CONCLUSION

We have demonstrated that the chain propagating potency of PAs was greatly enhanced through the introduction of a silyl group. The cationic polymerization of PAs proceeded smoothly in the presence of a superacid, CF_3SO_3H, to give polymers with moderate to high yields. The polymer structures were characterized by NMR, IR, UV−vis, GPC, and fluorescence spectroscopies, which showed that the polymers had a conjugated backbone with *trans*-configurations. Furthermore, based on the analysis of MALDI-TOF MS of polymers and NMR structural analysis of three kinds of oligomers, a plausible polymerization mechanism was proposed. Overall, this silicon promoted cationic polymerization of PAs represents a metal-free protocol to synthesize conjugated polymer in a convenient manner, which will shed new light on further researches related to functional PAs and expand the application scope of polymeric PAs in optical and electronic materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02191.

Detailed synthesis of monomers, characterization spectra of PAs and PPAs (PDF)

AUTHOR INFORMATION

Corresponding Authors

*Tel: +86-021-64253037. E-mail: hagmhsn@ecust.edu.cn (A.H.).
*Tel: +86-021-64252271. E-mail: yunding@ecust.edu.cn (Y.D.).

ORCID

Aiguo Hu: 0000-0003-0456-7269

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from National Natural Science Foundation of China (21674035 and 21474027), the Fundamental Research Funds for the Central Universities (22221818014), and Shanghai Leading Academic Discipline Project (B502). A.H. thanks the “Eastern Scholar Professorship” support from the Shanghai local government.

REFERENCES

(1) MacDiarmid, A. G. “Synthetic Metals”: A Novel Role for Organic Polymers (Nobel Lecture). *Angew. Chem., Int. Ed.* **2001**, *40*, 2581.

(2) Heeger, A. J. Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials. *J. Phys. Chem. B* **2001**, *105*, 8475.

(3) Shirakawa, H. The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers (Nobel Lecture). *Angew. Chem., Int. Ed.* **2001**, *40*, 2574.

(4) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene,(CH) x. *J. Chem. Soc., Chem. Commun.* **1977**, 578.

(5) Kang, E. T.; Bhatt, A. P.; Villaroel, E.; Anderson, W. A.; Ehrlich, P. Semiconductor properties of solution-doped polyphenylacetylene. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 143.

(6) San Jose, B. A.; Akagi, K. Liquid crystalline polyacetylene derivatives with advanced electrical and optical properties. *Polym. Chem.* **2013**, *4*, 5144.

(7) Tang, B. Z.; Chen, H. Z.; Xu, R. S.; Lam, J. W.; Cheuk, K. K.; Wong, H. N.; Wang, M. Structure-property relationships for photoconduction in substituted polyacetylenes. *Chem. Mater.* **2000**, *12*, 213.

(8) Zhao, H.; Yuan, W. Z.; Tang, L.; Sun, J. Z.; Xu, H.; Qin, A.; Mao, Y.; Jin, J. K.; Tang, B. Z. Hybrids of Triphenylamine-Functionalized Polyacetylenes and Multiwalled Carbon Nanotubes: High Solubility, Strong Donor-acceptor Interaction, and Excellent Photoconductivity. *Macromolecules* **2008**, *41*, 8566.

(9) Zeng, Q.; Cai, P.; Li, Z.; Qin, J.; Tang, B. Z. An imidazole-functionalized polyacetylene: convenient synthesis and selective chemosensor for metal ions and cyanide. *Chem. Commun.* **2008**, 1094.

(10) Kang, S. W.; Jin, S. H.; Chien, L. C.; Sprunt, S. Spatial and orientational templating of semiconducting polymers in a cholesteric liquid crystal. *Adv. Funct. Mater.* **2004**, *14*, 329.

(11) Qu, J.; Suzuki, Y.; Shiotsuki, M.; Sanda, F.; Masuda, T. 3-Butyl-2-yl-and Propargyl Cholesteryl Carbonates. Chiroptical and Liquid Crystalline Properties of their Polymers. *Macromol. Chem. Phys.* **2007**, *208*, 1992.

(12) Higashimura, T.; Masuda, T.; Okada, M. Gas permeability of polyacetylenes with bulky substituents. *Polym. Bull.* **1983**, *10*, 114.

(13) Liu, J.; Lam, J. W.; Tang, B. Z. *Synthesis and Functionality of Substituted Polyacetylenes*; Wiley-VCH: Weinheim, 2010.

(14) Das, T. K.; Prusty, S. Review on conducting polymers and their applications. *Polym.-Plast. Technol. Eng.* **2012**, *51*, 1487.

(15) Krivoshei, I.; Skorobogatov, V. *Polyacetylene and Polyarylenes: Synthesis and Conductive Properties*; Gordon and Breach: 1991.

(16) Furlani, A.; Iucci, G.; Russo, M.; Bearzotti, A.; D'Amico, A. Iodine-doped polyphenylacetylene thin film as a humidity sensor. *Sens. Actuators, B* **1992**, *8*, 123.

(17) Lam, J. W.; Tang, B. Z. Functional polyacetylenes. *Acc. Chem. Res.* **2005**, *38*, 745.

(18) Kiess, H. G. *Conjugated Conducting Polymers*; Springer: 1992; Vol. *102*.

(19) Masuda, T.; Hasegawa, K.-i.; Higashimura, T. Polymerization of Phenylacetylenes. I. Polymerization of Phenylacetylene Catalyzed by WCI6 and MoCI5. *Macromolecules* **1974**, *7*, 728.

(20) Masuda, T.; Higashimura, T. Synthesis of high polymers from substituted acetylenes: exploitation of molybdenum-and tungsten-based catalysts. *Acc. Chem. Res.* **1984**, *17*, 51.

(21) Masuda, T. Substituted polyacetylenes: synthesis, properties, and functions. *Polym. Rev.* **2017**, *57*, 1.

(22) Suslov, D.; Pakhomova, M.; Bykov, M.; Ushakov, I.; Tkach, V. Polymerization of phenylacetylene by cationic acetylacetonate palladium complexes. *Catal. Commun.* **2019**, *119*, 16.

(23) Natta, G.; Mazzanti, G.; Corradini, P. In *Stereoregular Polymers and Stereospecific Polymerizations*; Natta, G., Danusso, F., Eds.; Elsevier: 1967; p 463.

(24) Schrock, R. R.; Luo, S.; Zanetti, N. C.; Fox, H. H. Living Polymerization of (o-(Trimethylsilyl) phenyl) acetylene Using" Small Alkoxide" Molybdenum (VI) Initiators. *Organometallics* **1994**, *13*, 3396.

(25) Liaw, D. J.; Soum, A.; Fontanille, M.; Parlier, A.; Rudler, H. New metal carbenes as initiators of the polymerization of alkynes. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 309.

(26) Katz, T. J.; Lee, S. J. Initiation of acetylene polymerization by metal carbenes. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(27) Kern, R. J. Preparation and properties of isomeric polyphenylacetylenes. *J. Polym. Sci., Part A-1: Polym. Chem.* **1969**, *7*, 621.

(28) Angoy, M.; Jiménez, M. V.; García-Orduña, P.; Oro, L. A.; Vispe, E.; Pérez-Torrente, J. s. J. Dinuclear Phosphine-Amido [Rh2 (diene){μ-NH (CH2) 3PPh2} 2] Complexes as Efficient Catalyst Precursors for Phenylacetylene Polymerization. *Organometallics* **2019**, *38*, 1991.

(29) Zhou, H.; Zhao, B.; Fu, C.; Wu, Z.; Wang, C.; Ding, Y.; Han, B.-H.; Hu, A. Synthesis of Conjugated Microporous Polymers through Cationic Cyclization Polymerization. *Macromolecules* **2019**, *52*, 3935.

(30) Cruz, A. R.; Hernandez, M. C. G.; Guzmán-Gutiérrez, M. T.; Zolotukhin, M. G.; Fomine, S.; Morales, S. L.; Kricheldorf, H.; Wilks, E. S.; Cárdenas, J.; Salmón, M. Precision Synthesis of Narrow Polydispersity, Ultrahigh Molecular Weight Linear Aromatic Polymers by A2 + B2 Nonstoichiometric Step-Selective Polymerization. *Macromolecules* **2012**, *45*, 6774.

(31) Olvera, L. I.; Guzmán-Gutiérrez, M. T.; Zolotukhin, M. G.; Fomine, S.; Cárdenas, J.; Ruiz-Trevino, F. A.; Villers, D.; Ezquerra, T. A.; Prokhorov, E. Novel High Molecular Weight Aromatic Fluorinated Polymers from One-Pot, Metal-Free Step Polymerizations. *Macromolecules* **2013**, *46*, 7245.

(32) Kricheldorf, H. R.; Zolotukhin, M. G.; Cárdenas, J. Non-Stoichiometric Polycondensations and the Synthesis of High Molar Mass Polycondensates. *Macromol. Rapid Commun.* **2012**, *33*, 1814.

(33) Kasi, B.; Murugesan, V.; Kaliaperumal, N. Super acid-catalyzed polymerization of phenothiazine and modified isatin. *Appl. Petrochem. Res.* **2019**, *9*, 91.

(34) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. Directed electrophilic cyclizations: Efficient methodology for the synthesis of fused polycyclic aromatics. *J. Am. Chem. Soc.* **1997**, *119*, 4578.

(35) Senese, A. D.; Chalifoux, W. A. Nanographene and Graphene Nanoribbon Synthesis via Alkyne Benzannulations. *Molecules* **2019**, *24*, 118.

(36) Tummatorn, J.; Punjajom, K.; Rodphon, W.; Ruengsangtongkul, S.; Chaisan, N.; Lumyong, K.; Thongsornkleeb, C.; Nimnual, P.; Ruchirawat, S. Chemoselective Synthesis of 1,1-Disubstituted Vinyl Triflates from Terminal Alkynes Using TfOH in the Presence of TMSN3. *Org. Lett.* **2019**, *21*, 4694.

(37) Yang, Y.; Moschetta, E. G.; Rioux, R. M. Addition of Sulfonic Acids to Terminal Alkynes Catalyzed by a Rhodium Complex: Ligand Concentration-Controlled Reaction Selectivity. *ChemCatChem* **2013**, *5*, 3005.

(38) Yang, X.; Li, Z.; Zhi, J.; Ma, J.; Hu, A. Synthesis of Ultrathin Mesoporous Carbon through Bergman Cyclization of Enediyne Self-Assembled Monolayers in SBA-15. *Langmuir* **2010**, *26*, 11244.

(39) Zhao, P.; Wu, Y.; Feng, C.; Wang, L.; Ding, Y.; Hu, A. Conjugated Polymer Nanoparticles Based Fluorescent Electronic Nose for the Identification of Volatile Compounds. *Anal. Chem.* **2018**, *90*, 4815.

(40) Tietze, L. F.; Kinzel, T.; Wolfram, T. Asymmetric allylation of methyl ketones by using chiral phenyl carbinols. *Chem. - Eur. J.* **2009**, *15*, 6199.

(41) Hein, S. J.; Arslan, H.; Keresztes, I.; Dichtel, W. R. Rapid Synthesis of Crowded Aromatic Architectures from Silyl Acetylenes. *Org. Lett.* **2014**, *16*, 4416.

(42) Dhakal, B.; Bohe, L.; Crich, D. Trifluoromethanesulfonate Anion as Nucleophile in Organic Chemistry. *J. Org. Chem.* **2017**, *82*, 9263.

(43) Lee, B. E.; North, A. M. The polymerization of substituted acetylenes. Part I. The cationic polymerization of phenylacetylene. *Makromol. Chem.* **1964**, *79*, 135.

(44) Saragas, N.; Floros, G.; Paraskevopoulou, P.; Psaroudakis, N.; Koinis, S.; Pitsikalis, M.; Mertis, K. Polymerization of terminal alkynes with a triply bonded ditungsten halo-complex. *J. Mol. Catal. A: Chem.* **2009**, *303*, 124.

(45) Simionescu, C. I.; Percec, V. Thermal cis-trans isomerization of cis-transoidal polyphenylacetylene. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 147.

(46) Onoda, A.; Fukumoto, K.; Arlt, M.; Bocola, M.; Schwaneberg, U.; Hayashi, T. A rhodium complex-linked beta-barrel protein as a hybrid biocatalyst for phenylacetylene polymerization. *Chem. Commun.* **2012**, *48*, 9756.

(47) Summerville, R. H.; Senkler, C. A.; Schleyer, P. V. R. Solvolysis of vinyl triflates. Effect of alkyl substituents, solvents, and added nucleophiles. *J. Am. Chem. Soc.* **1974**, *96*, 1100.

(48) Matsidik, R.; Komber, H.; Luzio, A.; Caironi, M.; Sommer, M. Defect-free Naphthalene Diimide Bithiophene Copolymers with Controlled Molar Mass and High Performance via Direct Arylation Polycondensation. *J. Am. Chem. Soc.* **2015**, *137*, 6705.

(49) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc.: Wallingford, CT, 2009.

(51) Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580.

(52) Murray, J. S.; Politzer, P. The electrostatic potential: an overview. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2011**, *1*, 153.

(53) Politzer, P.; Murray, J. S.; Bulat, F. A. Average local ionization energy: a review. *J. Mol. Model.* **2010**, *16*, 1731.

(54) Lambert, J. B.; Wang, G. T.; Finzel, R. B.; Teramura, D. H. Stabilization of positive charge by. beta.-silicon. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

(55) Alabugin, I. V.; Manoharan, M. Effect of double-hyper-conjugation on the apparent donor ability of sigma-bonds: Insights from the relative stability of delta-substituted cyclohexyl cations. *J. Org. Chem.* **2004**, *69*, 9011.

(56) Alabugin, I. V. In *Stereoelectronic Effects: A Bridge Between Structure and Reactivity*; Alabugin, I. V., Ed.; John Wiley & Sons, Ltd.: Chichester, UK, 2016; p 42.

(57) Chen, S.; Li, Q.; Sun, S.; Ding, Y.; Hu, A. A Novel Approach toward Polyfulvene: Cationic Polymerization of Enediynes. *Macromolecules* **2017**, *50*, 534.

DOI: 10.1021/acs.macromol.9b02191