Convenient Synthetic Route to Tetraarylphosphonium Polyelectrolytes via Palladium-Catalyzed P–C Coupling of Aryl Triflates and Diphenylphosphine

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ABSTRACT: A series of eight tetraarylphosphonium polyelectrolytes (TPELs) has been successfully synthesized by polymerization of diphenylphosphine and bis(aryl triflate)s. The bis(aryl triflate)s are readily prepared from bisphenols, some of which are commodity feedstocks such as bisphenol A. The polymerization via palladium catalyzed P–C bond formation produces degrees of polymerization up to 65. All polymeric triflates have reasonable thermal stability in the range of 350–450 °C. The stability of the TPELs to alkaline solution is strongly depending on the spacer between adjacent phosphonium sites. Polymers with electron-releasing and bulky substituent *para*- to the phosphonium site have improved stability while those with electron-withdrawing substituent *para*- to phosphonium site have decreased alkaline stability due to decomposition via a nucleophilic aromatic substitution pathway. These findings have important ramifications for the design of ionomers for alkaline exchange membrane fuel cells and related electrochemical energy conversion devices. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

KEYWORDS: alkaline stability; ionomer; P–C coupling; phosphonium; polycondensation; polyelectrolytes; thermogravimetric analysis (TGA)

INTRODUCTION Polyelectrolytes have been attracting tremendous interest in recent decades due to the growing range of applications available based on their intriguing and unique properties.[1] Phosphonium-derivatized polyelectrolytes in particular have been investigated for application in diverse applications ranging from their use as antimicrobial agents and biodelivery vectors,[2–16] to materials and energy applications such as alkaline fuel cell membranes,[17–20] redox-active films,[21,22] ordered optically active materials[23–25] and optoelectronic devices.[26]

Compared to polyelectrolytes bearing *alkyl*phosphonium sites, *tetraaryl*phosphonium polyelectroplytes (TPELs) have demonstrated significantly improved thermal and chemical (particularly alkaline) stability.[27,28]

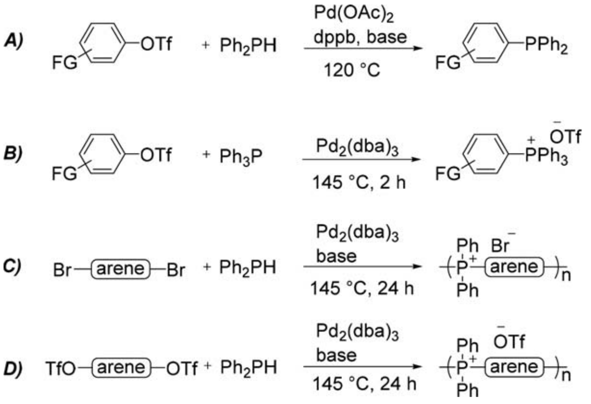
Because of the advantageous properties of TPELs and their potential in practical applications, we were inspired to develop simple and convenient polymerization routes to TPELs based on transition metal-catalyzed P–C coupling.

There are at present three reported methods to prepare TPELs: one requiring multistep postpolymerization modification,[29] and two methods involving the much more efficient transition metal-catalyzed P–C bond formation[28,30] similar to the route that is the focus of the current contribution.

In 2015, we reported the first transition metal-catalyzed P–C bond formation route to TPELs via coupling of bis(triarylphosphine) and aryl dihalide monomers.[28] The scope and potential for commercialization of this methodology is limited by the expensive, multistep methodologies required to prepare the requisite bis(triarylphosphine) monomers.[31] We recently reported a significantly simplified route to TPELs via direct Ni- or Pd-catalyzed P–C coupling polymerization of commercial aryl dihalides and diphenylphosphine [Scheme 1(C)].[27] The use of aryl dihalides, however, is still relatively expensive and the halide counteranions need to be exchanged for other anions (i.e., triflate ($^{-}$OTf) or ditriflamide (NTf_2^-)) to obtain the most thermally robust materials. It is thus of interest to develop direct routes to TPELs bearing triflate couteranions in a single-step process.

Triflate is a common leaving group in well-established transition metal-catalyzed C–C coupling reaction,[32,33] and more recently has found use in small molecule P–C coupling as

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Established P-C coupling to triarylphosphine (A) and tetraarylphosphonium salts (B). The reported coupling of aryl bromides with HPPh2 (C) inspired the new route to polymeric triflates (D).

well. In a 1996 report, Gilbertson et al. reported that aryl triflates can be converted to aryldiphenylphosphine derivatives in 80–90% yield employing a Pd^{II}-catalyst and diphenylphosphine [Scheme 1(A)].[34] Furthermore, in 2007, Charette's group reported that functionalized aryl triflates can be coupling efficiently with triphenylphosphine [Scheme 1(B)] to yield tetraarylphosphonium salts via a catalytic cycle summarized in Scheme 2.[35,36]

Charette further revealed that these coupling reaction are compatible with various functional groups including electron-donating groups and electron-withdrawing groups at positions *para*- and *meta*- to the coupling site. These promising small molecule proof-of-principle studies inspired us to explore coupling of aryl ditriflates with diphenylphosphine as a direct route to triflate TPELs [Scheme 1(D)]. In addition to eliminating the anion exchange step, the triflate monomers can be readily prepared from a wide variety of commercial bisphenol compounds. Bisphenols (notable bisphenol A (BPA)) are affordable and widely used in the industrial-scale production of polymers, and their facile, quantitative conversion to ditriflates via room-temperature esterification with triflic anhydride is well established.[37]

TABLE 1 General Properties of Triflate TPELs

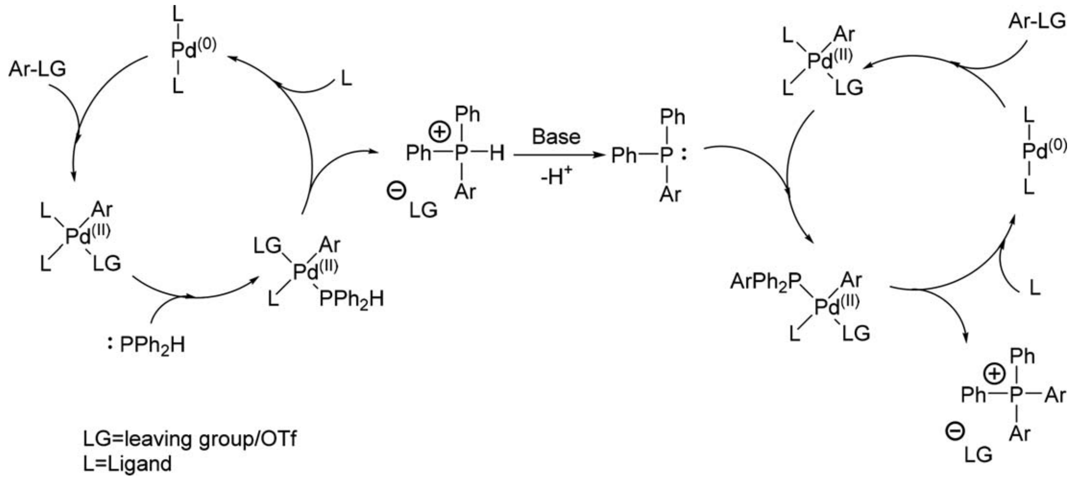
Polymer	M_n (kDa)	X_n	T_d (°C)	T_g (°C)
P1	34.4	65	433	251
P2	16.6	33	441	260
P3	27.8	47	415	N/A
P4	11.9	21	373	N/A
P5	18.2	28	362	N/A
P6	13.0	20	374	N/A
P7	16.5	30	355	N/A
P8	32.1	62	384	244

Herein, we report the development of a new P–C coupling route and its application to the preparation of eight structurally diverse triflate TPELs. The relationship between structure and the thermal and alkaline stability of the materials is also discussed.

EXPERIMENTAL

General Considerations

All air-sensitive manipulations were performed in an MBraun UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBraun solvent purifier. NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300, 75.5, 282, and 121 MHz for ^{1}H, ^{13}C, ^{19}F, and ^{31}P, respectively. Thermogravimetric analysis (TGA) was performed on TA Instruments SDT Q600 from 25 to 800 °C with a heating rate of 20 °C min^{-1} under a N$_2$ atmosphere. Differential scanning calorimetry (DSC) was performed on TA Instruments SDT Q600 with a heat/cool/heat cycle at 5 °C min^{-1}, and the T_g data reported in Table 1 are for the second scan (cooling and first/second heating curves are provided in the Supporting Information Fig. S42). UV–vis absorption spectra were acquired on a Cary 50 spectrophotometer. Phosphorus-31 NMR spectra were collected with a 10-s relaxation delay to obtain accurate integration of main chain versus end group



SCHEME 2 Proposed catalytic cycle for the P-C coupling reaction.

resonances. The instrument was referenced to phosphoric acid standard (0 ppm) and an additional PPh_3 external standard (-4.70 ppm) was employed to account for instrument drift.

Materials

Anhydrous ethylene glycol (99.8%, Sigma Aldrich), anhydrous pyridine (99.8%, Sigma Aldrich), 4,4′-(9-fluorenylidene) diphenol (97%, Sigma Aldrich), 4,4′-(1-phenylethylidene) bisphenol (99%, Sigma Aldrich), 4,4′-cyclohexylidenebisphenol (98%, Sigma Aldrich), 4,4′-thiodiphenol (99%, Sigma Aldrich), tris(dibenzylideneacetone)dipalladium(0) (97%, Sigma Aldrich), 4,4′-dihydroxydiphenyl ether (98%, TCI America), 4,4-dihydroxytetraphenylmethane (98%, TCI America), trimethylamine (99%, TCI America), 4,4′-sulfonyldiphenol (99.7%, ACROS), diphenylphosphine (99%, STREM Chemicals), triflic anhydride (97%, STREM Chemicals), lithium triflate (99%, STREM Chemicals), and dichloromethane (99.5%, BDH Chemicals) were used without further purification.

General Route for the Synthesis of Bis(triflate) Monomers

The general procedure that follows is based on a reported method.[37] To a 100-mL round bottom flask were added the requisite bisphenol (10.0 mmol) and anhydrous pyridine (40.0 mmol) dissolved in 10 mL dichloromethane (DCM) under a nitrogen atmosphere. The flask was cooled to 0 °C in an ice bath for 10 min and then a 10-mL DCM solution of triflic anhydride (40.0 mmol) was added slowly via cannula under a positive pressure of N_2. After stirring overnight, the reaction mixture was cooled in an ice bath and 20 mL water was added to quench any remaining triflic anhydride. The mixture was extracted with 100 mL DCM. The DCM layer was subsequently washed with 50 mL 2 *M* HCl(*aq*), 50 mL 1 *M* NaCl(*aq*) and 50 mL deionized water. The DCM phase was concentrated to 10 mL under reduced pressure and further purified by passage through a 5-cm high silica gel plug in a 30-mL fritted funnel to yield pure products. Yields and spectroscopic characterization data for each monomer follows.

4,4′-(Propane-2,2-Diyl)-Bis(Phenyl Triflate) (M1)

Yield: 4.85 g (98.5%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.16–7.30 (m, 8H), 1.69 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 150.2, 147.8, 128.7, 125.2, 121.1, 120.9, 116.6, 112.4, 43.0, 30.8

4,4′-Oxydiphenyl Bistriflate (M2)

Yield: 3.825 g (82.0%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.05–7.10 (m, 4H), 7.26–7.30 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 156.2, 145.3, 125.2, 123.2, 121.0, 120.4, 116.7, 112.5

4,4′-(1-Phenylethylidene)-(Bisphenyl Triflate) (M3)

Yield: 4.89 g (88.5%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.03–7.35 (m, 13H), 2.20 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 148.9, 148.0, 147.2, 130.5, 128.5 (d), 125.2, 121.0, 116.7, 112.4, 52.2, 30.7

4,4′-Cyclohexylidene-Bis(Phenyl Triflate) (M4)

Yield: 4.21 g (79.4%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.16–7.34 (m, 8H), 2.26 (d, 4H), 1,53 (br s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 148.3, 147.6, 129.1, 125.1, 121.3, 120.9, 116.7, 112.4, 46.1, 37.3, 26.1, 22.7

4,4′-(9-Fluorenylidene)-Bis(Phenyl Triflate) (M5)

Yield: 6.04 g (98.4%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.81–7.84 (d, 2H), 7.26–7.47 (s, 10H); 7.15–7.18 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 149.6, 148.5, 145.8, 140.1, 128.3 (d), 125.9, 125.3, 121.3, 120.9, 120.6, 116.6, 112.2, 64.4

4,4′-(Diphenylmethylene)-(bisphenyl triflate) (M6)

Yield: 6.13 g (99.4%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.12–7.36 (m, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 147.8, 146.6, 145.2, 132.8, 130.8, 128.0, 126.7, 120.8, 120.5, 116.6, 64.3

4,4′-Sulfonyldiphenyl Bistriflate (M7)

Yield: 5.07 g (98.6%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.45–7.50 (m, 4H), 8.06–8.11 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 152.7, 141.0, 130.4, 125.0, 122.8, 120.7, 116.5, 112.2

4,4′-Thiodipheyl Bistriflate (M8)

Yield: 4.79 g (99.2%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.25–7.30 (m, 4H), 7.40–7.45 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 148.8, 135.7, 132.6, 125.0, 122.5, 120.8, 116.6, 112.2

General Procedure for Polymerization

The requisite bistriflate monomer (2.69 mmol), diphenylphosphine (0.525 g, 2.82 mmol), diisopropylamine (0.274 g, 2.69 mmol) $Pd_2(dba)_3$ (0.0270 mmol, 0.0280 g), and 6 mL anhydrous ethylene glycol were mixed together in a 15-mL heavy-wall pressure tube sealed with a Teflon stopper and Viton O-ring under a nitrogen atmosphere. The sealed vessel was heated at 145 °C with stirring for 24 h. After cooling down to room temperature, the reaction vessel was opened to air and 50 mL DCM was added. The mixture was then washed with 0.5 *M* LiOTf(*aq*) (2 × 50 mL). The addition of triflate anions in the aqueous phase was undertaken as a precaution against any adventitious anion exchange. The organic layer was dried over anhydrous $MgSO_4$ and concentrated to 10 mL under reduced pressure by rotary evaporation. The crude solution was slowly poured into 200 mL diethyl ether with stirring to yield a cloudy suspension. The solid was separated by vacuum filtration and dried in a vacuum oven overnight at 60 °C to give the desired product. The structure of each polymer is provided in Scheme 2 and characterization for each member of the series follow.

P1

Yield: 0.947 g (69.4%). ^1H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.15–7.42 (br m, 18H), 1.88–1.61 (br, 6H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 25.52 (end groups), 24.42–21.54 (backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): -78.44. Anal. calcd for monomer formula $C_{28}H_{24}F_3O_3PS$ (ignoring end groups): C, 63.63; H, 4.58; found: C, 63.39; H, 4.60%

P2

Yield: 0.680 g (51.1%). ^1H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.03–7.69 (br m, 14H), 7.69–7.45 (br, 4H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 25.15 (ignoring end groups), 24.53–20.29

(backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): −78.52. Anal. calcd for monomer formula $C_{25}H_{18}F_3O_4PS$ (ignoring end groups): C, 59.76; H, 3.61; found: C, 60.02; H, 3.70%.

P3

Yield: 1.50 g (92%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.05–7.03 (br m, 23H), 2.36–2.13 (br, 3H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 24.86 (end groups), 23.60–21.46 (backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): −78.47. Anal. calcd for monomer formula $C_{33}H_{26}F_3O_3PS$ (ignoring end groups): C, 67.11; H, 4.44; found: C, 66.88; H, 4.50%.

P4

Yield: 1.29 g (81.4%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.13–6.95 (br m, 18H), 2.54–2.19 (br, 4H), 1.65–1.24 (br, 6H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 25.35 (end groups), 23.34–22.76 (backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): −78.49. Anal. calcd for monomer formula $C_{31}H_{28}F_3O_3PS$ (ignoring end groups): C, 75.33; H, 7.71; found: C, 74.13; H, 7.89%.

P5

Yield: 1.120 g (64.1%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.23–6.82 (br m, 26H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 25.35 (end groups), 24.13–21.98 (backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): −78.42. Anal. calcd for monomer formula $C_{38}H_{26}F_3O_3PS$ (ignoring end groups): C, 70.15; H, 4.03; found: C, 69.37; H, 4.27%.

P6

Yield: 1.50 g (85.5%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.09–7.42 (br, 18H), 7.37–7.02 (br, 10H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 26.21 (end groups), 23.61–21.20 (backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): −78.48. Anal. calcd for monomer formula $C_{38}H_{28}F_3O_3PS$ (ignoring end groups): C, 69.93; H, 4.32; found: C, 69.38; H, 4.64%.

P7

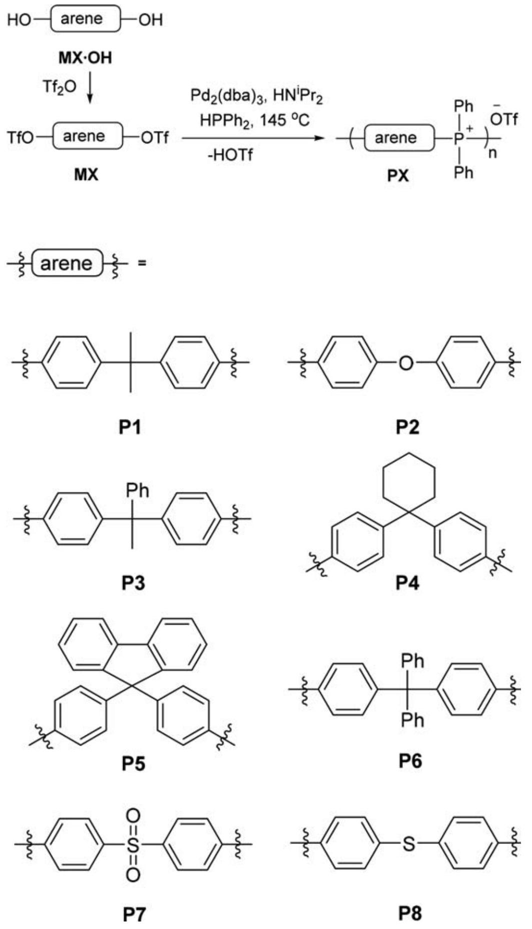
Yield: 0.719 g (50.6%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.52–6.94 (br m, 18H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 26.69 (end groups), 25.32–22.59 (backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): −78.63. Anal. calcd for monomer formula $C_{25}H_{18}F_3O_5PS_2$ (ignoring end groups): C, 54.54; H, 3.30; found: C, 57.02; H, 3.82%.

P8

Yield: 0.424 g (30.4%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ): 8.06–7.30 (br m, 18H); ^{31}P NMR (121 MHz, $(CD_3)_2CO$, δ): 25.51 (end groups), 24.62–22.42 (backbone phosphonium moieties); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, δ): −78.52. Anal. calcd for monomer formula $C_{25}H_{18}F_3O_3PS_2$ (ignoring end groups): C, 57.91; H, 3.50; found: C, 59.47; H, 3.71%.

Procedures for Alkaline Stability Testing

To a 50-mL round bottom flask was added a solution of 20 mg polymer powder dissolved in 0.2 mL DCM. The solution was evaporated slowly to coat a film homogeneously on the lower part of the inner wall of the flask. The polymer film was soaked in 1 *M* NaOH solution for 24 h. The organic material was extracted into 0.3 mL CH_2Cl_2, and 0.2 mL $(CD_3)_2CO$ was added. This solution was characterized by NMR spectrometry. The protocol was repeated at 65 °C, with the only difference being that the solution was cooled to room temperature prior to extraction. Each trial of alkaline stability test was done in duplicate and the percentage of decomposition (% decomp.) data provided in Table 3 are the average values.



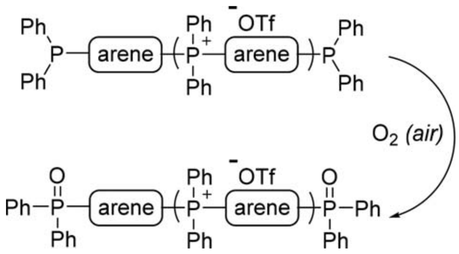
SCHEME 3 Synthesis of polymeric triflates.

RESULTS AND DISCUSSION

Synthetic Design and Characterization

The goal of the current work was to develop a P–C bond-forming route for the convenient preparation of tetraarylphosphonium polyelectrolytes (TPELs) using bis(aryl triflate)s and diphenylphosphine as the monomers.

On the basis of prior work in which different catalysts were evaluated for the preparation of TPELs,[27] tris-(dibenzylideneacetone) dipalladium(0) ($Pd_2(dba)_3$) was selected for the current work as well. Eight bisphenols bearing different functional groups were selected as starting materials for the bis(aryl triflate) monomers (Scheme 3). In order to evaluate the scope of the synthetic route, monomers that contribute electron-releasing substituents (as in **P2** and **P8**), electron-



SCHEME 4 Features of TPELs showing the formation of the phosphine oxide end groups used in calculation of degree of polymerization.

withdrawing groups (as in **P6**), and a range of steric hindrance to conformational freedom (i.e., **P1** vs. **P3-5**) were targeted.

Polymerization reactions were carried out in anhydrous ethylene glycol because of its success in high-yield P–C coupling to form small molecular tetraarylphosphonium salts and its ability to solubilize previously reported TPELs.[2,36,38]

Polymerization of diphenylphosphine (1.05 equiv) with **M1-M8** (1.00 equiv) catalyzed by $Pd_2(dba)_3$ at 145 °C in ethylene glycol thus led to successful preparation of the target triflate TPELs as summarized in Scheme 3.

The polymers were initially characterized via ^1H, ^{19}F, and ^{31}P NMR spectra. The absence of a ^{31}P NMR resonance for diphenylphosphine (a doublet at -41.00 ppm)[39] in crude mixtures confirmed the consumption of $HPPh_2$. Likewise, ^{19}F NMR spectrometry confirms complete consumption of aryl-bound triflate units (appearing at about -74.0 ppm) and that ionic triflate groups (appearing at about -78.5 ppm)[36,37] are the only fluorine-containing species detectable by NMR analysis (see Supporting Information Figs. S25–32).

Polyelectrolytes and related polymers can have very high affinity to GPC columns, sometimes requiring highly polar solvents such as formic acid for their elution.[28,40,41] Following the techniques previously reported,[42–44] NMR endgroup analysis was therefore selected as a convenient method to determine the M_n of the TPELs.

When equimolar amount of the bis(aryl triflate) and diphenylphosphine monomers were employed in the polymerization both aryl triflate end groups (evident in ^{19}F NMR spectra) and phosphine oxide (evident in ^{31}P NMR spectra) were observed. To simplify NMR endgroup analysis, a slight excess of diphenylphosphine monomer was employed, thus insuring that the end groups will be comprised almost entirely of phosphine moieties (confirmed by NMR spectra provided in the Supporting Information) that, upon aerobic workup, are transformed into phosphine oxide units (Scheme 4). This end group composition allowed for convenient determination of M_n via ^{31}P NMR end group analysis (Table 1). Accurate ^{31}P NMR integrations were obtained by using a 10-s delay between scans following the reported procedure.[30] As expected, each polymer's ^{31}P NMR spectrum features a major resonance consistent with main chain phosphonium salt and a significantly smaller resonance consistent with a phosphine oxide. The main chain phosphonium resonance for **P1–P8** is in the range of 20.29–25.32 ppm (Table 2) and the phosphine oxide end group is in the range of 24.86–26.69 ppm. The phosphonium and phosphine oxide resonances of **P7** are both slightly down field of those for other known TPELs due to the presence of the electron-withdrawing sulfonyl substituent *para-* to the phosphorus nuclei.

TABLE 2 Phosphorus-31 NMR Chemical Shifts for P1-P8

Polymer	δ of Phosphonium (ppm)	δ of End Group (ppm)
P1	22.87	25.52
P2	23.21	25.15
P3	23.08	25.32
P4	22.76	25.35
P5	23.02	25.35
P6	22.64	26.21
P7	24.41	26.69
P8	23.55	25.51

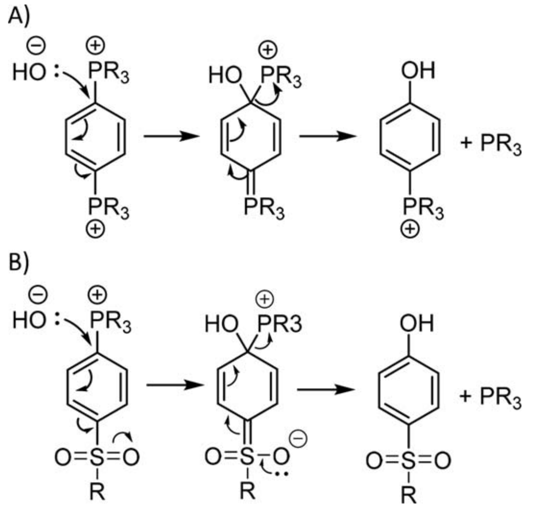
TABLE 3 Stability of Polymeric Triflates Upon Exposure to Aqueous Alkaline Solutions for 24 h

Polymer	% Decomp. (20 °C)	% Decomp. (65 °C)
P1	11	67
P2	4	18
P3	10	72
P4	23	23
P5	20	22
P6	3	10
P7	55	88
P8	17	60

The observed M_n values (Table 1) span a range from ~12 to 34 kDa, similar to those for TPELs prepared by coupling of $HPPh_2$ with aryl bromides. The variability of M_n for the isolated polymers appears to depend more on the relative solubility of lower molecular weight fractions that are removed in the precipitation step than on the efficiency of the polymerization process itself, as crude analysis suggests that polymers as-formed have M_n of about 20 prior to workup. An M_n of about 20 is expected on the basis of the monomer feed ratios employed, assuming an essentially quantitative coupling efficiency. Polymer **P2** was identified as a particularly attractive candidate for scaleup, so a 10-g sample of **P2** was prepared to assess the scalability of the process. The synthetic efficiency and molecular weight of the larger batch of **P2** were essentially identical to those of the smaller batch (see Supporting Information Fig. S42B).

Thermal Stability and Transitions

Davis and coworkers[45] demonstrated that tetraarylphosphonium salts are the most thermally stable ionic liquids known, so it was of interest to evaluate the thermal stability of **P1-**



SCHEME 5 Mechanism of decomposition for some phosphonium segments.

P8, and to study the effect of different repeat unit composition on thermal stability. Thermogravimetric analysis (TGA) was employed to determine the decomposition temperature (T_d) for each polymer. These data are summarized in Table 1.

Our previous work revealed that the counteranion has a significant effect on thermal stability of TPELs.[27] In one case, for example, the TPEL having ditriflamide counteranions exhibited a T_d of ~460 °C while its bromide analogue had a T_d of 400 °C. In addition to the counteranions, thermal stability should also be affected by the backbone composition.

Neutral polymers bearing spacers identical to those between phosphonium units in **P1**-**P8** all have excellent thermal stability ($T_d > 400$ °C)[46–50] and so their presence was not expected to diminish the inherent thermal stability of their composite TPELs. As anticipated, the T_d values for **P1**-**P8** are all relatively high, ranging from 355 to 441 °C. The lowest thermal stability is for **P7**. The diminished stability is attributable to the presence of two strongly electron-withdrawing groups on the same phenylene unit, an effect that has been observed in similarly substituted TPELs previously.[28]

Analysis of DSC data revealed that none of polymeric triflates has detectable glass transitions in the range of 20–200 °C. X-ray powder diffraction patterns for **P1**-**P8** revealed that all the polymers are amorphous, consistent with the results from DSC.

Chemical Stability

The chemical stability of all TPELs has been investigated upon exposure to 1 *M* NaOH(*aq*) at room temperature and 65 °C. The percentage of phosphonium moieties that undergo decomposition in **P1**-**P8** are summarized in Table 3.

Decomposition of 1,4-bis(triarylphosphonium)phenylene units upon exposure to alkaline solution is known to proceed via the S_NAr mechanism depicted in Scheme 5(A).[28] The SNAr mechanism is facilitated by the presence of an appropriate leaving group positioned either *ortho*- or *para*- to a strongly electron-withdrawing substituent on an aryl ring. This is the situation in **P7**, which consequently undergoes the greatest decomposition, with 55% decomposition occurring after only 24 h at room temperature, which we attribute to via the pathway shown in Scheme 5(B). Decomposition of related ammonium polyelectrolytes has been misattributed to the inherent instability of sulfone units to hydroxide.[51] In contrast to **P7**, **P2** has electron-releasing units *para*- to the phosphonium center and has significantly improved stability under alkaline conditions.

UV–Vis Absorption

The maximum absorption peaks in the UV–vis absorption spectra for **P1**-**P8** are located in the 220–230 nm range, attributable to the π-π^* transition of the backbone aryl units.[38] These data agree with the fact that TPELs do not exhibit extended π-conjugation along the backbone.[27] In addition to the π-π^* transition, the spectra for **P2** and **P8** exhibit absorptions at 268 and 300 nm, respectively. These can be attributed to n-π^* transitions involving the oxygen- (**P2**) or sulfur- (**P8**) centered lone pairs.

CONCLUSIONS

A P–C bond-forming route to TPELs from bis(aryl triflates) and diphenylphosphine is reported. Eight triflate TPELs have been prepared via this route and their thermal and alkaline stability has been assessed. The polymerization route has been proven compatible and effective for a range of functional groups of interest in polymeric materials, including a sulfone, ether, and thioether. The TPELs have good thermal stability up to 441 °C. A relationship between the chemical composition of the backbone and the susceptibility of these materials to decomposition under alkaline conditions has been revealed. Tests of these materials as anion exchange membranes for alkaline fuel cell applications are currently underway.

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