High Performance and Multipurpose Triarylamine-Enchained Semifluorinated Polymers

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ⓢ *Supporting Information*

ABSTRACT: Transparent, film-forming fluorinated arylene vinylene ether (FAVE) polymers with enchained triarylamine (TAA) moieties were prepared and characterized. Control over fluoro-olefin content within the backbone, as a function of base, was confirmed and postpolymerization dehydrofluorination was shown to increase fluoroolefin content from 5 to 31 mol %. Thermal cross-linking was found to occur approximately 100 °C lower than in traditional FAVE polymers (ca. 160 °C). Electrochemical analysis demonstrated the enchained TAA retained its established electrochemical character. The latent reactivity of the TAA was explored via electrophilic aromatic substitution and formylation reactions toward precise functionalization for specific electro-optic applications and others.
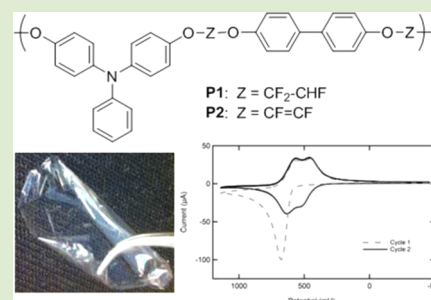
The concept of utilizing polymeric-based materials in photonic devices has garnered attention for several decades due to the promise of significant reductions in production costs compared to traditional inorganic materials.[1−4] However, challenges associated with the integration of organics into existing technologies, while retaining manufacturability, have limited adoption. Specifically, achieving high-speed, efficient operation while maintaining high chemical and thermal stability, necessitated by the device manufacturing process, has proven difficult.[5−8] For electro-optic devices, thermal degradation of electro-optic chromophores during processing often leads to increased optical loss and reduction in electro-optic (EO) activity. Polymers, such as APC, are often utilized as matrices to fix EO chromophores in poled, acentric orientations while also shielding their degradation.[7] Fluoropolymers are excellent candidates as EO matrix materials due to their impressive thermal stability, low optical loss, and chemical resistance.[9−11] Additional thermal stability can be attained through the formation of thermosets which are known to be more thermally and solvent resistive than thermoplastics, but are often difficult and expensive to manufacture at scale.[12] Thus, fluoropolymers which can cross-link during processing are desirable for EO and microelectronics applications and also in specialized lithography applications.

Fluorinated arylene vinylene ether (FAVE) polymers have been recently explored as passive hosts for a number of optically active species and serve as a versatile platform for this study.[13] To this FAVE platform an active triarylamine (TAA) moiety was enchained due to its well established hole-transport ability, known optical activity, utility as a donor for electro-optic chromophores, and photovoltaics.[14−18] In contrast to our platform polycondensation chemistry with perfluorocycloal-

kenes (PFCA), FAVE polymers allow for more versatile cross-linking known to date. Thus, we demonstrate a synthetic approach to polymerize and subsequently cross-link high-functionality materials, during additional processing, to create a class of potentially useful electro-optic devices for next generation optical signal manipulation. Herein we report the synthesis and characterization of a series of polymers with enchained TAA units via step-growth nucleophilic addition of TAA bisphenols to bisfluoroalkenes to achieve high molecular weight, film forming polymers.[19−21]

The bis(methoxy)triarylamine (**1**) and deprotected monomer (**2**) were prepared following standard literature procedure via Ullman coupling and BBr_3 methoxy deprotection, respectively.[15,22] Polymerization of **P1** was achieved using standard procedures for the nucleophilic addition of alcohols to bis-TFVE (trifluorovinyl ether) monomers (Scheme 1).[20] Polymers were synthesized employing Cs_2CO_3 (**P1**) or NaH (**P2**) to bias the polycondensation product toward fluoroalkane (**P1**) or fluoroalkene (**P2**) linkages, respectively.[20] Polymer **P1** was obtained with excellent molecular weight (M_n 35 KDa) and low fluoroalkene content (5% of linkages), whereas **P2** gave lower molecular weight (M_n 12 KDa) and significantly higher fluoroalkene content (98% of linkages). The lower molecular weight of **P2** compared to **P1** is due to slight variations in the stoicheometric equivalence of NaH to bisphenol. It is worth noting that while **P1** forms tough flexible films, **P2** does not, most likely arising from the lower molecular weight and greater rigidity of **P2** compared to **P1**.

Scheme 1. Synthesis of 1, 2, P1, P1a, P1b, P2, and P3[a]
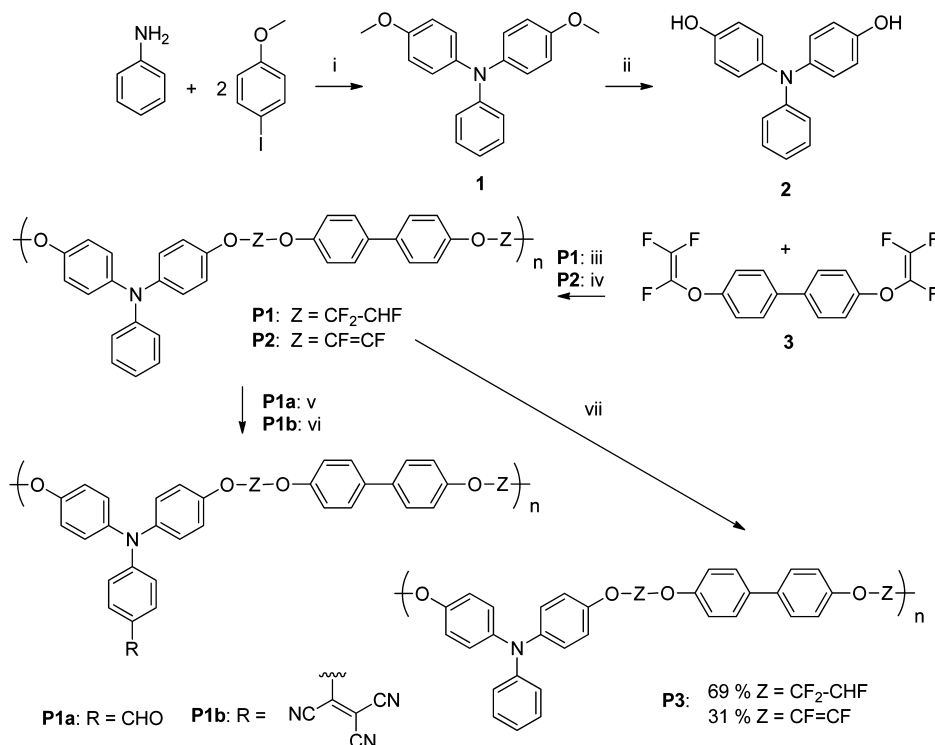
[a]Reagents and conditions: (i) CuCl, phenthroline, KOH, toluene, reflux, 12 h; (ii) BBr$_3$, CH$_2$Cl$_2$, 0–20 °C, 5 h; (iii) **2**, **3**, Cs$_2$CO$_3$, DMF, 60 °C, 24 h; (iv) **2**,**3**, NaH, DMF 80 °C, 24 h; (v) POCl$_3$, CH$_2$Cl$_2$, RT, 24 h; (vi) TCNE, DMF, RT, 12 h; (vii) NaH, DMF, 100 °C, 16 h.

The ^{19}F NMR spectra of these polymers are distinctive and inform the geometries of these systems (Figure 1). The
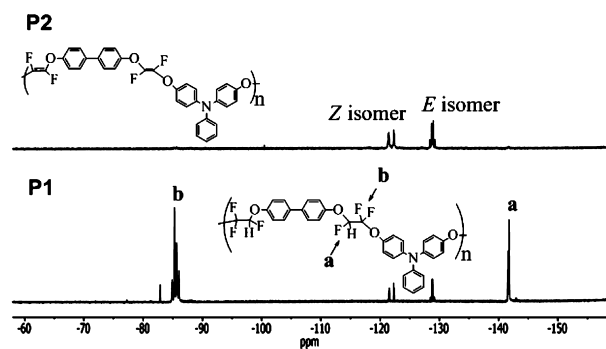

Figure 1. ^{19}F NMR spectra indicate polymers **P1** and **P2**.

fluoroalkene linkage of **P2**, as shown in Figure 1, contains a doublet of doublets appearing at δ −122 ppm corresponding to the Z conformation at the olefinic bond while the doublet at δ −129 ppm is assigned to the E conformation.[20] The fluoroalkane (**P1**), on the other hand, has major peaks at δ −85 ppm and δ −142 ppm arising from the addition product of the bisphenol to the TFVE monomer, while a small fraction of the unsaturated fluoro-olefin also forms (less than 5% of linkages).

Postpolymerization functionalization (e.g., chromophorization − functionalizing an inert polymer backbone into an active EO chromophore enchained polymer) is a useful tool to impart added functionality to a polymeric system. We have demonstrated three distinct reactions, including dehydrofluorination, formylation, and electrophilic aromatic substitution

(EAS) reactions (Scheme 1). Dehydrofluorination of the fluoroalkane linkages to fluoroalkenes with non-nucleophilic base NaH has been previously reported for small molecules and some polymeric systems, such as PVDF, but has yet to be demonstrated in functionalized FAVE polymers.[23,24] Here, for the first time, we emphasize the application of this technique on FAVE polymers and, particularly, **P1**. Action of NaH on **P1** produced **P3**, wherein the fluoro-olefin content of the resultant polymer was increased 6-fold, from 5% (in **P1**) to 31% (in **P3**). This transformation is illustrated in Figure 2 where ^{19}F NMR spectroscopy is employed to monitor the reaction progress (optimized conditions between fluoro-olefin conversion and chain degradation were found to occur at 100 °C for 16 h in DMF). The spectrum, taken at 8 h intervals, shows the gradual increase in fluoroalkene content until the reaction is stopped after 16 h; longer reaction times led to increased degradation of the polymer by the NaH and were avoided.

Additionally, formylation and EAS of **P1** were achieved to demonstrate the synthetic versatility of the TAA unit postpolymerization. The aldehyde of **P1a** can be utilized in a range of synthetic chemistries including extension into an electro-optic chromophore, a facsimile of which has been reported in small molecule form.[18] **P1b** represents general EAS type reactions that can be utilized to functionalize this system. All of these reactions are high yielding, which extends the overall versatility of this polymeric system.

UV−vis spectroscopic studies were performed to explore the effect of varying fluoroalkane/alkene content upon the electronic properties, and thus reactivity, of the TAA moiety. There was no significant change observed in the absorption spectra of the triarylamine moiety for **P1**, **P2**, or **P3**. The spectra, taken in chloroform, displayed two absorptions corresponding to the $\pi−\pi^*$ transitions of the BP (260, 260,
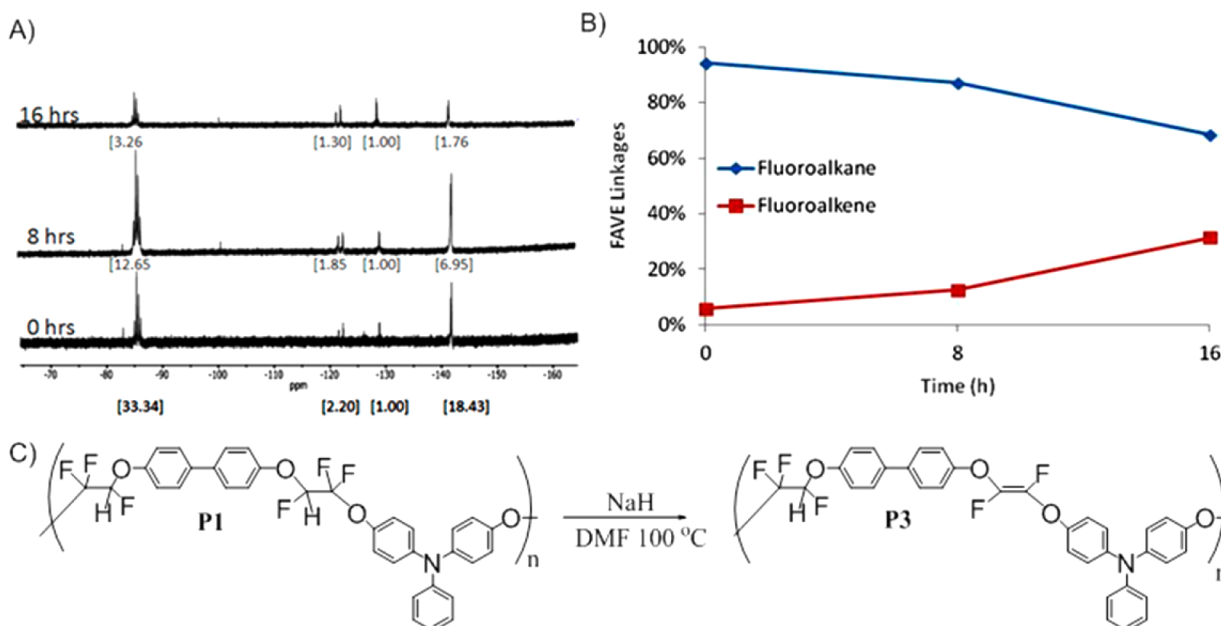
Figure 2. (a) ¹⁹F NMR spectra show the dehydrofluorination of **P1** (synthesis of **P3**). Increasing fluoro-alkene content with dehydrofluorination time is observed. (b) Percentage of fluoroalkane and fluoroalkene in the total sample as a function of time. (c) Reaction scheme of **P1** to **P3**.

258 nm) and TAA (299 nm, 297 nm, 299 nm) moieties for **P1**, **P2**, and **P3**, respectively. This suggests that the electronic structure of the π system of the TAA moieties is robust and generally independent of fluoroalkene content.

Electrochemical analysis of **P1** was performed to explore the effect of enchainment on the redox properties of the TAA unit. The voltammogram of **P1** (Figure 3) shows a single large oxidation at 688 mV followed by two smaller reduction waves in the cathodic sweep. Subsequent cycles revealed the presence of two reversible redox couples at $E_{1/2}$ = 608 and 510 mV, and the absence of the peak at 688 mV. This behavior matches
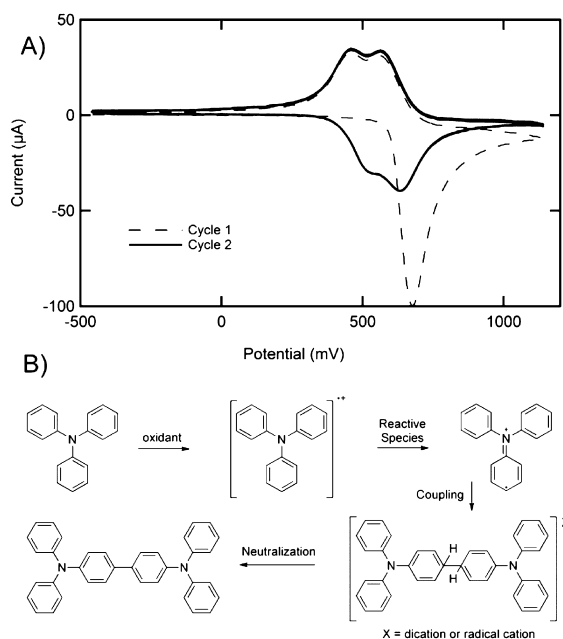

Figure 3. (a) Thin film cyclic voltammogram of **P1** (drop cast on working electrode). Values are cited against Fc/Fc⁺ internal reference. (b) General oxidative coupling scheme for triarylamines.

literature reports of triarylamine oxidation and dimerization.[25] The initial large oxidation indicates the formation of the radical cationic species and the oxidative and reductive waves correlate to the complex first and second redox process for the electrochemically reversible dimer. This coupling reaction results in intramolecular cyclization or intermolecular cross-linking between polymer chains.

The physical properties of **P1**, **P2**, and **P3** have been summarized in Table 1. The impressive degradation temperatures (T_d, calculated at 5% mass loss) up to 450 °C, for **P1**, are typical of FAVE polymer systems. The onset of degradation for the polymers with higher concentration olefinic backbone, **P2** and **P3** appear at 350 °C and are likely due to oxidation of the fluoroolefin bonds. Degradation was however, very slow spanning over a 300 °C range (see Supporting Information). Overall char yields of approximately 60%, or higher in most cases were observed for these systems.

DSC studies on the thermal properties of **P1** and **P2** reveal well-defined glass transitions at 120 and 115 °C, respectively. Heating to 200 °C for several cycles caused the T_g of **P2** to shift dramatically, while the T_g of **P1** shifted only about 10 °C (Figure 4). This effect was explored by annealing a sample of **P1** and **P2** at 140−160 °C for 1 h. Gel fractions of 5, 95, and 65% for **P1**, **P2**, and **P3**, respectively, track well with the fluoro-olefin content of the polymers. This observation leads to the supposition that fluoroalkene content and, thus, the dehydro-fluorination reaction described for the formation of **P3** can be utilized to tailor the extent of network formation in these systems. This supposition is further evidenced by solid state fluorine and carbon NMR spectroscopy (SS ¹⁹F NMR and SS ¹³C NMR), which reveal that the total fluorine content remains unchanged during cross-linking, while the fluoroalkene (double bond) signal disappears after cross-linking, suggesting that the fluoroalkene reacts during this annealing process (see Supporting Information). It is noteworthy that significant gel formation was obtained for all polymers at the elevated temperature of 240 °C, as commonly observed and expected with polymers possessing biphenyl units.[26]

Table 1. Summary of Molecular Weight and Thermal Properties of Polymers P1–P3

polymers	M_n (KDa)	M_w (KDa)	PDI	$T_d{}^a$ (°C)	$T_g{}^b$ (°C)	fluoroalkene content (%)	gel fraction (%) 160 °C/1 h	gel fraction (%) 240 °C/1 h
P1	35	81	2.3	420	120	5	<5	90
P2	12	19	1.6	350	115	98	95	98
P3	25	43	1.7	350	115	31	65	90

^{a}TGA taken at 10 °C/min rate up to 800 °C under N_2. ^{b}DSC taken at 10 °C/min rate under N_2.
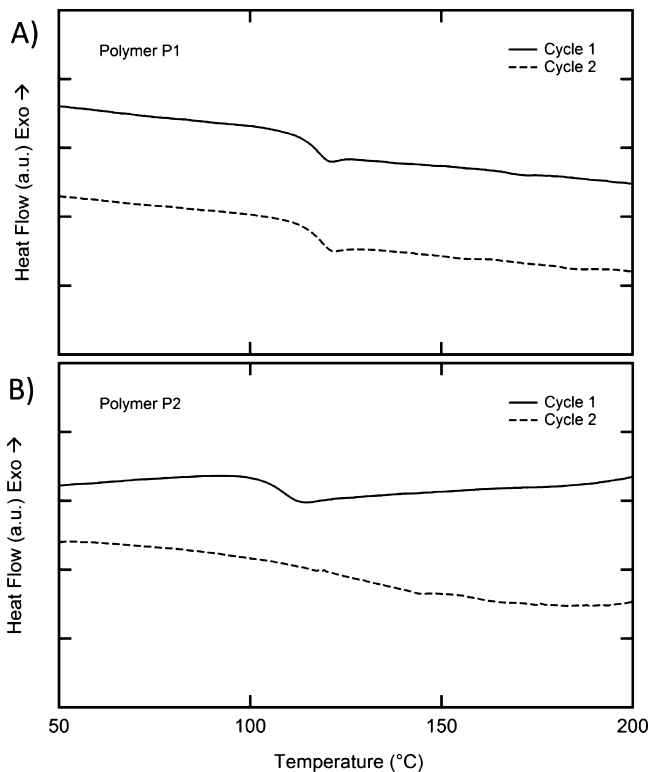

Figure 4. (A) DSC thermogram for **P1** showing a T_g at 120 °C for 2 heating cycles. (B) DSC thermogram for **P2** showing the heating cycle only for 2 cycles at a 10 °C/min rate. Cycle 2 shows the slight increase (A) or loss of (B) a distinct T_g after isothermally cross-linking at 160 °C/1 h.

We have successfully synthesized and characterized a unique class of FAVE polymers with TAA enchainment. These polymers are synthetically versatile, have controllable fluoroalkene content and are cross-linkable by discrete thermal or electrochemical pathways. For the first time, we demonstrated dehydrofluorination of fluoroalkane linkages in specifically functionalized FAVE polymers. Future work will focus on mechanistic studies on the cross-linking of these materials as well as their incorporation into photonic devices.

EXPERIMENTAL SECTION

Materials, instrumentation, and the synthesis of **P1**, **P2**, **P3**, **P1a**, and **P1b** are given in the Supporting Information. Synthesis of **1** and **2** were described previously in the literature (the synthetic procedure and characterization is given in the Supporting Information).[15,22]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for all molecules as well as supporting spectra may be found. 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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