Polymer Chemistry

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Journal:	*Polymer Chemistry*
Manuscript ID	PY-ART-02-2024-000149.R1
Article Type:	Paper
Date Submitted by the Author:	17-Jul-2024
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Journal Name

COMMUNICATION

One-pot Single-step Copolymerization of Aromatic Trifluorovinyl Ethers toward Perfluorocyclobutyl (PFCB) Segmented Copolymers†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We report a selective [2 + 2] cyclo-copolymerization of aryl trifluorovinyl ethers (TFVEs) toward segmented copolymers. Experimental and computational studies confirm that copolymerization of relatively electron-rich and electron-poor TFVE monomers results in segmented copolymers in a single polymerization. The effect of microstructures on post-sulfonation in the polymer backbones was also investigated.

Perfluorocyclobutyl (PFCB)-containing polymers are a special class of semi-fluorinated poly(aryl ethers) (PAEs) targeted for a wide range of applications such as force-responsive materials,[1] high-performance coatings,[2, 3] electro-optics,[4-6] photonics,[7-9] and fuel cells.[10-20] Although the most well-established materials are highly processable and tailorable PFCB homopolymers,[21-25] which are synthesized via step-growth [2 + 2] cyclo-polymerization of aromatic triflurovinyl ether (TFVE) monomers, copolymers and other architectures have also been described extensively in the literature.[7,26] In most cases, PFCB copolymers were found to be random in nature[7] and monomer sequence control has been neglected due to presumed TFVE reaction rate similarities and the statistical nature of step-growth polymerization mechanisms.[27] A need exists for well-defined PFCB copolymers that provide a wide variability of polymer structures for which the chemical nature may be understood and controlled, allowing for the rational design of materials *via* chemical reactions at the polymer backbones. Precise control of the monomer distribution in copolymers would not only provide opportunities for understanding the unique properties of copolymers[28-30] but also offer a means of controlling polymer morphology, e.g., *via* post-modification and/or self-assembly of sequence-controlled functional copolymers.[31-36] For example, the selective functionalization of sequence-controlled copolymers could create a material having well-defined pathways for ion transport in energy devices such as fuel cells and photovoltaic cells.

To this end, Tetramer Technologies, L.L.C. and General Motors reported PFCB aryl ether copolymers with segmented repeat units containing sulfonic acid groups for proton exchange membrane fuel cells (PEMFCs).[14-17] Relative to homopolymer membranes, a marked improvement was observed in the proton conductivity and mechanical properties of the membranes made from the selectively sulfonated hydrophilic-hydrophobic segmented copolymers. However, there was no explicit evidence of segmented structures in the copolymers provided other than excellent fuel cell performance after multiple hydration cycles (0-100% humidity).[14] The results indicated that phase separated continuous micro-channels with extreme proton conductivity protected by a robust fluorocarbon matrix were assembled – like Nafion™-type PEMFC – due to the segmented copolymer microstructure.[15–17] Furthermore, multi-step polymerizations were required to synthesize the PFCB segmented copolymers and at least one pre-made oligomer was needed.

We herein describe the realization of a facile synthetic route for segmented PFCB aryl ether copolymers synthesized directly from two aryl trifluorovinyl ether (TFVE) monomers having different reactivities. The hexafluoroisopropyl (6F)

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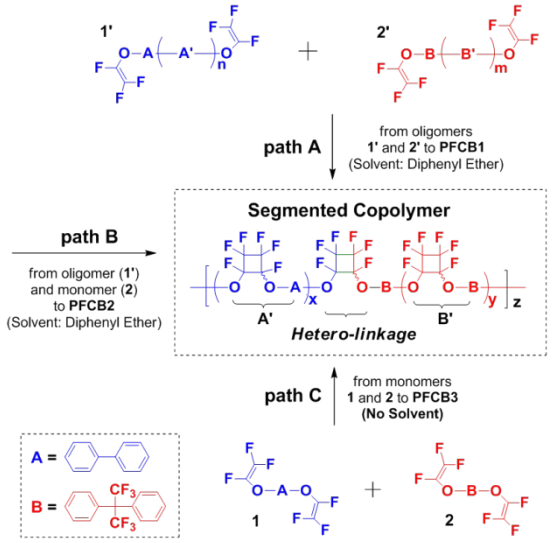
†Electronic Supplementary Information (ESI) available: Synthetic procedures and characterization of the materials: ^{1}H and ^{19}F NMR, TGA, DSC, EA, and computational data. See DOI: 10.1039/x0xx00000x

monomer is less reactive toward cyclopolymerization compared to a biphenyl monomer (BP) due to its electron-withdrawing effect.[4] This allows segments of PFCB biphenyl to grow faster compared to the 6F segments. Once the concentration of BP monomer decreases, segments of 6F are expected to form. We provide evidence for segmented copolymer structures using ^{19}F nuclear magnetic resonance (NMR) spectroscopic data. Along with the selective copolymerization, the effect of the copolymer



Scheme 1 Thermal [2 + 2] cycloaddition reactions of TFVEs toward segmented copolymers.

microstructure on sulfonation selectivity is also discussed. To the best of our knowledge, this report contains the first realization of selective [2 + 2] cyclo-copolymerization of TFVE monomers toward segmented PFCB copolymers and the first characterization of monomer sequence distribution in PFCB copolymer chains.

Scheme 1 illustrates a PFCB aryl ether copolymer architecture consisting of two different segments (e.g., A' and B') with hetero-linkages between them. Three different PFCB aryl ether copolymers were prepared and are designated as **PFCB1**, **PFCB2**, and **PFCB3**. The copolymers were synthesized using a combination of (i) two different oligomers (**1'** and **2'**, Path A, **PFCB1**), (ii) oligomer and monomer (**1'** and **2**, Path B, **PFCB2**), and (iii) two different monomers (**1** and **2**, Path C, **PFCB3**), respectively. These syntheses are straightforward and may be performed on a large scale with high efficiency and technical simplicity. The [2 + 2] cycloaddition without catalyst or initiator is favored thermodynamically for TFVE due to an increased double-bond strain, a lower C=C π-bond energy, and the strength of the resulting fluorinated C-C single bond adducts in contrast to hydrocarbon analogs.[23,37-39] This synthetic methodology does not demand a multi-step process such as protection-deprotection cycles to obtain segmented copolymers. Furthermore, the preparation of oligomers is not necessary for segmented copolymers. Our version of a [2 + 2] step-growth cyclo-copolymerization was performed *via* selective cycloaddition reactions of two aryl TFVE monomers, where monomer **1** contains a biphenyl (BP) group and monomer **2** incorporates an electron-withdrawing hexafluoro-*i*-propyl (6F) group between two phenyl rings, as shown in Scheme 1, path C.

This synthetic route allows quantification of the degree of polymerization by monitoring changes in the relative

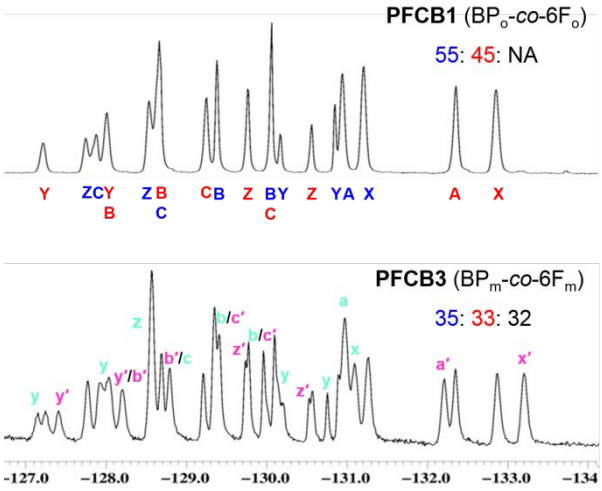
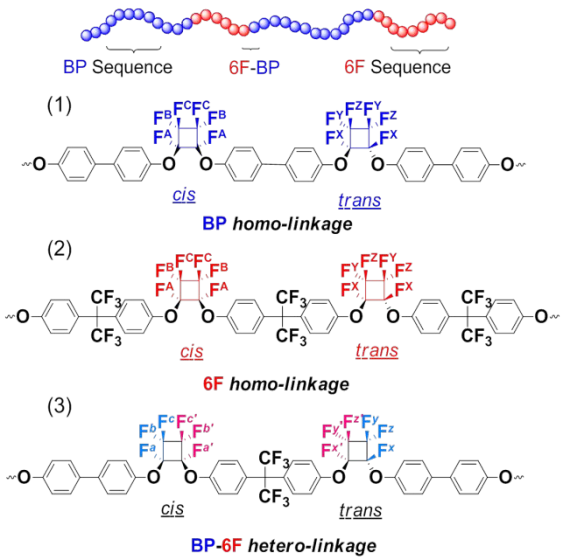


Fig. 1 The ^{19}F NMR (in $CDCl_3$) spectra of **PFCB1** and **PFCB3.** The ratio of homo- and hetero-linkages of the copolymer chain is displayed as BP-BP:6F-6F:BP-6F. Blue corresponds to fluorine peaks of the PFCB moieties on the BP homo-linkage, while red corresponds to those on 6F homo-linkage, and light blue and pink correspond to those on the hetero-linkages, as defined in Scheme 2.



Scheme 2 Illustration of diastereomeric PFCB ethers.

intensity of the fluoro-olefin end groups and PFCB moieties by ^{19}F NMR spectroscopy end-group analysis.[23] The *cis/trans* diastereomeric ratio of PFCB ether moieties[40, 41] and the

Table 1 Compositional ratios of PFCB aryl ether copolymers

Copolymer [a]	BP:6F [b]		Sequence distribution(%) [c]		
	Feeding	NMR	BP-BP	6F-6F	BP-6F
PFCB1 (BP_o-*co*-$6F_o$)	35:65	55:45	55	45	NA
PFCB2 (BP_o-*co*-$6F_m$)	59:41	53:47	53	44	3
PFCB3 (BP_m-*co*-$6F_m$)	50:50	50:50	35	33	32

[a] BP_m = BP monomer, BP_o = BP oligomer (M_n= 8 kDa), 6Fm = 6F monomer, and $6F_o$ = 6F oligomer (M_n= 15 kDa). [b] Molar ratio of the BP and 6F repeating units estimated from the initial feeding amount of reagents and ^{19}F NMR spectroscopic data of resulting copolymer, respectively. [c] Monomer sequence distribution determined by ^{19}F NMR, where BP-BP, 6F-6F, and BP-6F refer to the BP homo-linkage, 6F homo-linkage, and BP-6F hetero-linkage, respectively.

compositional ratios for the BP and 6F repeat units in the PFCB copolymer chains may also be simply measured by ^{19}F NMR spectroscopy (Fig. S2†). Remarkably, the monomer sequences were also found to affect the chemical shift for fluorine signals in the resulting PFCB isomers. The PFCB moieties produced *via* co-dimerization were clearly distinguished from the homo-dimerized PFCB rings in ^{19}F NMR spectra (Fig. 1). Scheme 2 illustrates the three possible homo- and hetero-linkage types for the BP and 6F repeat units formed by head-to head cyclization. All three linkages were identified as *cis*/*trans* (50:50) isomers, and the fractional values of the hetero-linkages and homo-linkages in the copolymers were estimated from the intensities of their peaks (Fig. 1 and Table 1). We note that the thermally initiated [2+2] cyclization proceeds via a radical mechanism, not a concerted pericyclic reaction. Therefore, it generally occurs in a head-to-head fashion that produces the most stable diradical intermediate, it also affords less than 5% of the head-to-tail (1,3-substituted) PFCB units.[22] Even though, the signals of the head-to-tail arrangement in the ^{19}F NMR are buried with the predominant signals of the head-to-head PFCB units, these data are highly useful for understanding monomer distribution in the PFCB copolymer structures.

As noted earlier, two pre-made PFCB oligomers may combine to produce segmented copolymers (Scheme 1, Path A). The resultant **PFCB1** (BPo-*co*-6Fo) was a segmented copolymer composed of a negligible BP-6F hetero-linkage with 55% BP homo-linkage and 45% 6F homo-linkage (Fig. 1). A different segmented copolymer (**PFCB2**) was also prepared through selective-copolymerization of BP oligomers (**1'**) and 6F monomer (**2**) in a one-pot single copolymerization. The segmented copolymer (**PFCB2**) formation was confirmed by ^{19}F NMR, showing only a small portion of BP-6F hetero-linkage (3%). We note that these quantitative studies using ^{19}F NMR spectroscopic data provide the first explicit evidence of the blocky copolymer structure. In general, selective copolymerization tends to occur when the co-monomer ratio is very low and, predictably, the cycloaddition of monomers occurs faster than oligomers due to steric and spatial orientation restraints.[38] The relatively rapid homo-polymerization of 6F monomers results in block or segmented **PFCB2** copolymer.

In the case of copolymer **PFCB3** prepared by Path C, at an equal molar ratio of monomers, the high co-monomer concentration at early polymerization stages leads to decreased selectivity for homo-dimerization, thus leading to a more random monomer distribution in the copolymer. For this reason, co-polymerization of two TFVE monomers has previously been thought to produce random copolymers. A truly random copolymer would have a BP-BP:6F-6F:BP-6F linkage ratio of 1:1:2. However, we find that the copolymerization of BP monomers and 6F monomers produced a 1:1:1 linkage ratio, as shown in Fig. 1, suggesting a segmented copolymer with a 2:1 preference for homo-linkages relative to hetero-linkages, or an average segment length of three monomers. Scheme S3† illustrates the rationalization of copolymer types (e.g., block, segmented, random, and alternating copolymer) along with the linkage ratios. These experimental data provide the first evidence for segmented copolymer formation from TFVE monomers *via* selective copolymerization in a single polymerization.

The selective copolymerization results for **PFCB2** and **PFCB3** are consistent with previous kinetic studies for the [2 + 2] cycloaddition of aromatic trifluorovinyl ethers considering electronic and steric effects.[4,38] Spraul *et al.* reported second-order rate constants for cyclodimerization of aryl TFVE with various substitutions using a Hammett treatment to correlate reactivity with substituents.[4] The calculated reaction constant (ρ) values are –0.46 at 120°C and –0.59 at 130°C, which implies that TFVE monomers hold a large charge separation in their transition state (TS). Therefore, the 6F monomer, which contains an electron-withdrawing group between the phenyl rings, destabilizes the TS and leads to a higher energy barrier between the reactants and diradical intermediate, resulting in lower reactivity toward cyclodimerization than for the BP monomer. The 6F monomer has been successfully employed to attenuate the reactivity of hexakis(trifluorovinyloxy)-hexabenzocoranene for variable copolymer networks.[42]

To help explain the reactivity and selectivity of cycloaddition reactions of the fluoro-olefins (e.g., **1** and **2**), the barrier heights for these cycloaddition reactions were computationally studied using several density functional theory (DFT) methods.[4,43] All calculations were performed without solvent effects, reflecting the solvent-free conditions in the experimental study of path C despite monomer acting as a reactive diluent. Transition state structures were located at the B3LYP/6-31G(d) level of theory.[43-47] Monomer structures **S1** and **S2** (Scheme 3) included only one TFVE group, rather than two, to reduce computational costs but included both phenyl rings of the BP and 6F structures to account for the electron-withdrawing effect. Two distinct conformations of the transition states (TS) were found corresponding to a *cis* or *trans* configuration relative to the cyclobutyl ring once formed. These states have only negligible differences in energy; however, the barrier heights associated with the formation of TS-S11 are 27.8 kcal mol^{-1} and 28.0 kcal mol^{-1} corresponding to the *cis* and *trans* TS, respectively. The two reactions involving **S1** present lower activation barriers than the homo-dimerization between **S2** with barrier heights of 28.0 kcal mol^{-1} for TS-S11, 28.1 kcal mol^{-1} for TS-S12, but 43.4 kcal mol^{-1} for TS-S22. To confirm this finding and rule out any effects from the DFT method or basis set used, single-point energies of the B3LYP/6-31G(d)-optimized transition state geometries were obtained at five additional levels of theory: B3LYP/6-31+G(d),[43-48] B3LYP/6-311++G(d,p),[43-48] mPW1PW91/6-31G+(d,p),[45-49] ωB97X/cc-pVTZ,[50-53] and M062X/6-31+G(d,p).[45-49, 54] The same trend in the activation energies was consistently observed with all methods (Table S1†), i.e., the activation energies corresponding to the formation of TS-S11 and TS-S12 are very similar and are ~10–17 kcal mol^{-1} lower than that of TS-S22. These results suggest that, based only on the barrier energies, the homo-dimerization of BP is expected to be faster than the homo-dimerization of 6F. This finding is consistent with the experimental observation of selectivity leading to non-random segmented copolymers.

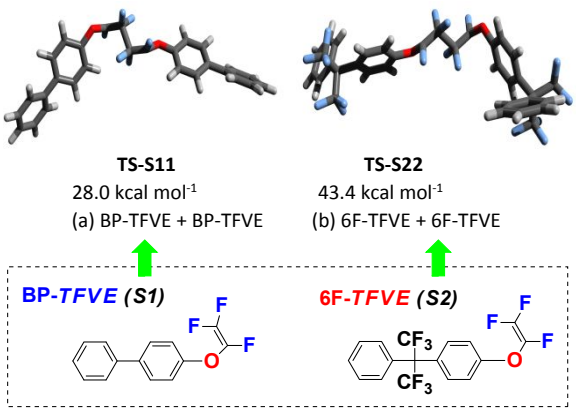
Consequently, the reactivity that is influenced by electronic and steric factors can be listed in the following order: BP monomer (BP_m) > 6F monomer ($6F_m$) > BP oligomer (BP_o) > 6F oligomer ($6F_o$). Therefore, the cyclopolymerization reaction kinetics in the preparation of PFCB aryl ether copolymers can be described as follows: Path A - **PFCB1**: BP_o-*ho*-BP_o > BP_o-*co*-$6F_o$ > $6F_o$-*ho*-$6F_o$, Path B - **PFCB2**: $6F_m$-*ho*-$6F_m$ >> $6F_m$-*co*-BP_o > BP_o-*ho*-BP_o, and Path C - **PFCB3**: BP_m-*ho*-BP_m ≳ BP_m-*co*-$6F_m$ > $6F_m$-*ho*-$6F_m$, where *-ho-* and *-co-* refer to homo-dimerization and co-dimerization, respectively. The effect of this varying reactivity on the copolymer composition is illustrated in Scheme S2†. Although the segment length in PFCB3 is short when compared with **PFCB1** and **PFCB2**, the current results indicate the possibility of controlling segment length by adjusting the reactivity differences of monomers and/or *via* sequential monomer addition.[55, 56]

Table 2 Selected properties of PFCB aryl ether copolymers

Copolymer	GPC[a]			T_g[b]/°C	T_d[c]/°C
	M_n/ g mol^{-1}	M_w/ g mol^{-1}	PDI		
PFCB1 (BP_o-*co*-$6F_o$)	27000	59000	2.14	114	470
PFCB2 (BP_o-*co*-$6F_m$)	32000	66000	2.06	119	471
PFCB3 (BP_m-*co*-$6F_m$)	38000	91000	2.39	127	464

[a] Gel permeation chromatography (GPC) in $CHCl_3$ using polystyrene as standard. [b] Differential scanning calorimetry (DSC) (10°C/min) in nitrogen determined by second heating cycle. [c] 5% weight loss based on thermal gravimetric analysis (TGA) (10°C/min) of polymers in nitrogen.

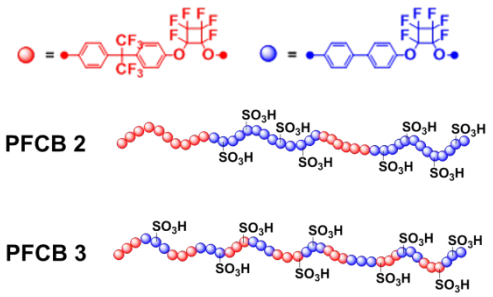
The number-averaged molecular weights of the copolymers were estimated by size-exclusion chromatography and are listed in Table 2. The lower M_n (27 kDa) of **PFCB1** may be due, in part, to known crystallinity[41] and low solubility of the long-chain 6F oligomer along with its low reactivity, whereas copolymerization with the 6F monomer, producing **PFCB2** and **PFCB3**, shows higher M_n (32 and 38 kDa, respectively). We note that the high M_n of **PFCB3** was obtained under solvent-free reaction conditions. Thermal gravimetric analyses (TGA) exhibited good thermal stability for all three segmented copolymers (Table 2 and Fig. S4†). Fig. S5† presents a differential scanning calorimetry (DSC) thermogram of PFCB segmented copolymers. The glass transition temperature (T_g) of **PFCB1** is 114°C. Moreover, the DSC trace exhibits a broad exothermic peak around T_c = 165°C assigned to crystallization, followed by a second endothermic peak around T_m = 190°C, which is attributed to melting of the polymers. These peaks at T_c and T_m are indicative of the crystallinity in **PFCB1** due to the long 6F segments derived from a pre-made oligomer. On the other hand, **PFCB2** and **PFCB3** exhibited an amorphous nature, showing only a single T_g peak at 119 and 127°C, respectively. Although the segments of the given copolymers **PFCB2** and **PFCB3** have different lengths, with **PFCB3** having shorter segments, larger changes in the DSC analysis are not expected. Multiblock copolymers of BP-PFCB with poly(phenylene sulfide sulfone), obtained by multi-step polymerization, for proton exchange membrane



Scheme 3 Optimized TS structures of diradical intermediate homo-dimers.

applications have recently exhibited a single T_g value without significant variation when the length of the blocks is changed.[57] The semi-crystalline (**PFCB1**) and amorphous (**PFCB2** and **PFCB3**) copolymers were highly soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, and tetrahydrofuran (THF).

These highly processable and thermally stable PFCB aryl ether copolymers provided good candidates for further transformation. For example, electrophilic aromatic substitution reactions of phenyl rings provide a facile tailorable methodology for incorporating functional groups onto polymer chains.[58] Exploiting this advantage, PFCB polyelectrolytes were prepared by aryl group sulfonation to investigate the potential utility of ionomers for PEMFCs. The PFCB aryl ether



Scheme 4 Sulfonation Selectivity on PFCB2 and PFCB3.

copolymers (**PFCB2** and **PFCB3**) were sulfonated using chlorosulfonic acid, as described in Fig. S6†. The **PFCB2** block copolymer showed outstanding sulfonation selectivity, as illustrated in Scheme 4. Due to the electron-withdrawing 6F group, these segments are electronically deactivated toward electrophilic aromatic substitution reactions. The ^{1}H NMR results (Fig. S6†) demonstrate that post-sulfonation occurred selectively at the ortho position of the phenyl rings on the BP segment. On the other hand, **PFCB3** did not exhibit highly selective sulfonation because of the high proportion of hetero-linkages. Sulfonation was observed in all phenyl rings in the BP segment and the BP-6F hetero-linkage, except at the *meta* position of the 6F unit. Our observations on the selectivity of post-sulfonation illustrate the importance of understanding and controlling monomer distributions in the copolymer structures. The degree of sulfonation (DS) of **PFCB2** and **PFCB3**, determined from NMR analysis, elemental analysis, and titration was used to estimate ion-exchange capacity is reported elsewhere and reproduced in Table 3.[14-18] The effect of the microstructure and segment chain length on the polyelectrolyte properties will be reported separately.

Table 3 Ion-exchange capacity values for sulfonated PFCB copolymers

Copolymer	DS^a	$IEC_{NMR}{}^b$ (meq/g)	$IEC_{EA}{}^c$ (meq/g)	$IEC_{Tit}{}^d$. (meq/g)
PFCB2 (BP_o-*co*-$6F_m$)	0.42	2.25	2.04	2.05
PFCB3 (BP_m-*co*-$6F_m$)	0.26	1.26	1.75	1.63

[a] Degree of sulfonation determined by ^{1}H NMR, [b] IEC_{NMR} calculated using DS [a,c] IEC_{EA} calculated using sulfur content from sulfur content determined by EA,

In summary, high-molecular-weight PFCB aryl ether segmented copolymers were obtained in solvent-free, catalyst-free, and initiator-free polymerization reactions. The direct segmented copolymer formation from oligomer/ monomer or monomer/monomer paths in single copolymerization reactions was confirmed using ^{19}F NMR spectroscopy and clearly shows that the copolymers are segmented. Like with Nafion™ and other fluoropolymer electrolytes, the segments are ill-defined yet enable electrophillic micro-channels of extreme acidity and proton conductivity surrounded and reinforced by a robust hydrophobic semi-crystalline fluorocarbon matrix of 6F and non-sulfonated biphenyl repeat unit dominated segments.[15-17] This is the first report demonstrating selective step-growth copolymerization of fluoro-olefins with different reactivities that describes the monomer distributions in PFCB aryl ether copolymers. These findings extend the range of PFCB chemistry toward designing and/or developing novel PFCB copolymers, tuning microstrucutures by using the reactivity differences of monomers and/or by controlling the monomer feeding ratios. Further detailed investigations regarding the computational kinetic studies of TFVE monomers are in progress.

Acknowledgement

Financial support of this research by the US Department of Energy Award #DE-FG02-08ER46501 and South Carolina EPSCoR program (Jiyoung Park and Dennis Smith), the US Department of Energy, Office of Basic Energy Sciences, Geosciences and Biosciences Division under Award #DE-FG02-05ER15718 (Stephen Creager and Jung-Min Oh), and the Clemson CITI program (Steven Stuart and Tugba G. Kucukkal for computational work) is gratefully acknowledged. Tetramer Technology L.L.C. is gratefully acknowledged for donation of the TFVE bisphenol monomers and oligomers.

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- The data supporting this article have been included as part of the Supplementary Information.