Received: 22 March 2022 | Revised: 5 May 2022 | Accepted: 7 May 2022
DOI: 10.1002/pol.20220161

RESEARCH ARTICLE

JOURNAL OF POLYMER SCIENCE WILEY

Renewable isosorbide-enchained semi-fluorinated aromatic ether polymers

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Funding information
Mississippi State University, Grant/Award Number: 1852527

Abstract

Isosorbide-based renewable semi-fluorinated polymers were synthesized via base-mediated step-growth polycondensation of isosorbide diol monomer with *bis*-trifluorovinyl ether (TFVE) monomer in excellent yields. As the first example employing secondary alcohols in this addition/elimination polymerization affording fluorinated arylene vinylene ether (FAVE) polymers, reasonable to high-molecular weights (10–84 kDa) and reproducible glass transition temperatures (T_g) ranging from 120 to 130°C were achieved. Containing 23–31 wt.% renewable isosorbide repeat unit, the amorphous polymers are processable in common organic solvents and form tough, transparent films. Depending on basic conditions, these renewable semi-fluorinated polymers contain reactive fluoroalkene enchainment for post-polymerization functionalization and further retain the ability to thermally crosslink without the need for catalysts or initiators. Structural characterization of this complex asymmetric polymer was determined by multi-nuclear NMR including multiple 2D-NMR techniques. Renewable FAVE chemistry based on isosorbide presents an intriguing option for alternative renewable materials containing fluorine.

KEYWORDS

2D NMR, FAVE, fluoroalkenes, isosorbide, renewable polymers, step-growth polymerization, trifluorovinyl aromatic ether

1 | INTRODUCTION

Polymers containing fluorine are desired as high-performance materials for extreme (mean) environments due to their high-thermal stability, low-dielectric constant, good chemical resistance, and low-surface energy.[1–3] Such high-performance materials play important roles in coatings, elastomers, optoelectronics, proton-exchange membrane, and biomedical applications.[4–6] Unlike traditional/fully-fluorinated polymers, semi-fluorinated polymers are more solution and melt-processable and can maintain certain desired properties of perfluoropolymers.[7]

Our research group has focused on the synthesis and applications of tailored semi-fluorinated aromatic ether polymers prepared via step-growth polymerization, as shown in Figure 1. The fluorinated linkages in polymer include perfluorocyclobutyl (PFCB),[8,9] perfluorocycloalkenyl (PFCA),[10] and fluorinated arylene vinylene ether (FAVE).[11] Varying the spacer 'R' group shows tunability in the polymer properties for desired applications (Figure 1).[12] PFCA and FAVE polymers are obtained via base-mediated nucleophilic addition/elimination reaction of bisphenol with perfluorocyclohexene/pentene and *bis*-trifluorovinyl ether (TFVE), respectively.[13–16] However, PFCB polymers are prepared by [2 + 2]-radical-mediated thermal cyclopolymerization of TFVE substituted monomers.[17]

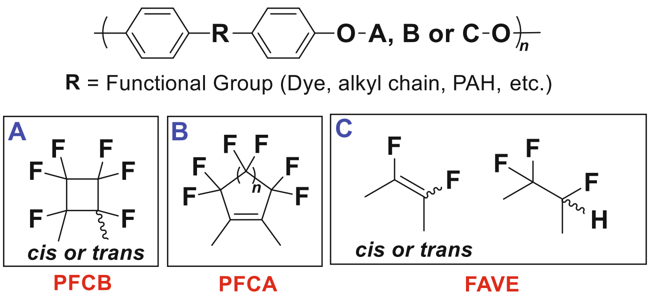


FIGURE 1 Generalized features of semi-fluorinated aromatic ether polymers containing perfluorocyclobutyl (PFCB), perfluorocycloalkenyl (PFCA), and fluorinated arylene vinylene ether (FAVE) functionalities

Isosorbide is a renewable diol derived from glucose[18] and arguably one of the best sustainable monomers to produce materials approaching engineering plastic performance.[19–21] Owing to the locked rigid bicyclic stereochemistry and synthetic versatility of isosorbide, its reactivity as a diol for polymerization with established *bis*-trifluorovinyl aromatic ether (TFVE) monomers to produce semi-fluorinated arylene vinylene ether (FAVE) polymers was pursued. Although bisphenols have been commonly employed to produce FAVE polymers, a few examples using primary aliphatic diols have been reported.[22–25] However, there are no previous reports of attempts to employ secondary or cyclic aliphatic diols to produce fluorinated arylene vinylene ether (FAVE) polymers. Herein, we report a facile, metal-free, and efficient step-growth polymerization of commercial isosorbide with *bis*-TFVE monomers to generate FAVE polymers containing a significant (23–31 wt.%) renewable and potentially biodegradable content. Semi-fluorinated polymers of this type may find application in the coating, optical film, and gas separation technologies.

2 | EXPERIMENTAL

2.1 | General procedures

All reagents were obtained from commercial suppliers and, unless specified, were used as received. Isosorbide was purchased from Oakwood chemicals, SC, USA, and was further purified by melt-recrystallization for polymerization. Sodium hydride (NaH), cesium carbonate (Cs_2CO_3), anhydrous DMF were purchased from Acros Organics. The monomers, 4,4′-(perfluoropropane-2,2-diyl)bis(([1,2,2-trifluorovinyl]oxy)benzene) and 4,4′-bis([1,2,2-trifluorovinyl]oxy)-1,1′-biphenyl were generously donated by Tetramer Technologies, LLC, Pendleton, SC.

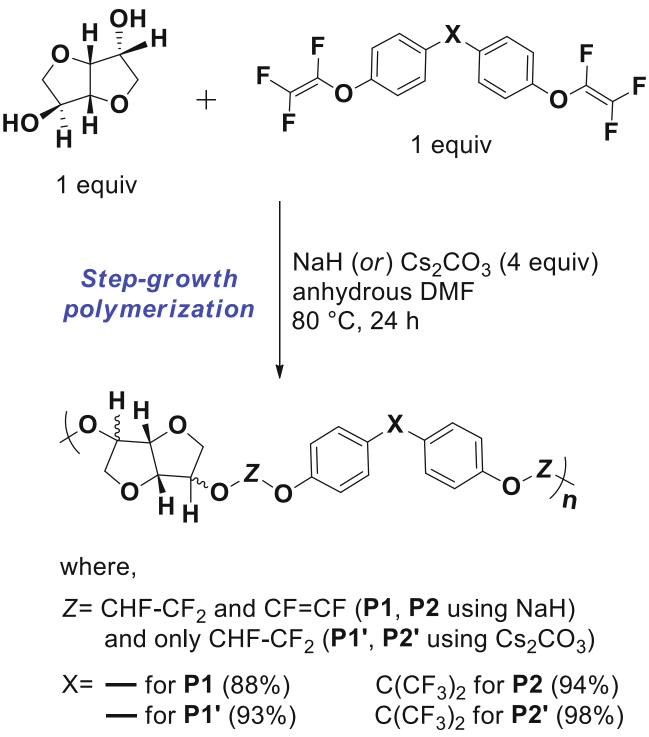
2.2 | Characterization and instrumentation

All NMR spectra were measured on a Bruker AVANCE III 500 MHz instrument using chloroform-*d* ($CDCl_3$) or dichloromethane-d_2 (CD_2Cl_2) as a solvent with all chemical shifts reported in parts per million (δ ppm). Fourier transform infrared (FTIR) spectroscopy experiments were conducted using an Agilent Cary 630 spectrophotometer with a diamond crystal ATR sample head between the wavelengths 4000 and 400 cm^{-1}. The experiments were carried out at a resolution of 2 cm^{-1}, and 128 scans were carried out for each sample. Differential scanning calorimetric (DSC) was performed on TA Q20 V4 instrument. Approximately 4–8 mg of the polymer was placed in TA low-mass aluminum pan, sealed, and a heat–cool-heat cycle (four heating and four cooling cycles) was employed between the temperatures of 0 and 400°C at a scanning rate of 10°C/min. Polymer glass transition temperatures (T_g) were obtained on the third heat-cool-heat cycle of DSC analysis. The raw data was extracted using TA universal analysis software V4.5a, and the plots were created using OriginPro 2018. Gel permeation chromatography (GPC) was performed to measure molecular weight using an Acquity gel permeation chromatograph at 35°C, equipped with Malvern Omnisec Reveal detector system. HPLC grade tetrahydrofuran (THF) was used as the eluting solvent at a flow rate of 1 ml/min. The molecular weights (M_n, M_w, and M_z) were obtained by calibrating against polystyrene standards based on the retention times monitored by a UV detector ($\lambda = 254$ nm).

2.3 | Preparation of polymers

2.3.1 | Synthesis of polymer P1

To a suspension of NaH (181.3 mg, 4.0 mmol) in DMF (0.5 ml), a solution of isosorbide (200 mg, 1 mmol) in DMF (0.5 ml) was added at room temperature. To this mixture, solution of 4,4′-bis([1,2,2-trifluorovinyl]oxy)-1,1′-biphenyl (473.8 mg, 1 mmol) dissolved in anhydrous DMF (0.5 ml) was transferred via syringe. This mixture was stirred for 1 h at room temperature, then heated to 45°C for 2 h, with subsequent increase in heat to 80°C for 15 h. An increase in viscosity was observed and additional DMF was added to maintain stirring. Aliquots were taken for GPC analysis and the reaction was stopped when molecular weight ceased to advance. The polymer was precipitated in MeOH/H_2O (1:1), filtered, and washed sequentially with deionized water (20 ml × 3), and hexane (10 ml × 3). The solid polymer was then dried in a vacuum oven at 50°C for 48 h. Additional purification was performed by dissolving dried polymer in a minimal amount of THF and precipitated in deionized water, filtered, and washed sequentially with water (10 ml × 3), and hexane (10 ml × 3). The solid polymer was then dried in a vacuum oven at 60°C for 24 h to afford **P1** as fibrous white solid (88% yield). Additional details of these procedures and characterization data are described in the Supporting information S1.



SCHEME 1 Step-growth polymerization of isosorbide with *bis*-TFVE derivatives to afford polymers **P1–P2** (using sodium hydride) and **P1′–P2′** (using cesium carbonate).

3 | RESULTS AND DISCUSSION

Scheme 1 illustrates the base-mediated step-growth polymerization of renewable isosorbide with *bis*-TFVE monomer to produce novel fluorinated arylene vinylene ether (FAVE) polymers **P1–P2** (using sodium hydride) and **P1′–P2′** (using cesium carbonate) in 88%–98% isolated yields after precipitation into MeOH/H_2O (50:50). After limited optimization, including solvent, temperature, and alternative bases (e.g., K_2CO_3 with or without 18-crown-6), Cs_2CO_3 gave the best results perhaps due to its greater solubility. Reasonably high-molecular weights with PDI values close to two were obtained as expected for the linear step-growth mechanism and selected properties are exhibited in Table 1.

Scheme 2 depicts the base-assisted nucleophilic addition of isosorbide to the electrophilic aryl TFVE group giving the anionic intermediate, which can eliminate fluoride to form the alkene (e.g., **P1**, **P2** using NaH) or be protonated to form saturated semi-fluorinated (—CHF—CF_2—) linkages in polymers (e.g., **P1′**, **P2′** using Cs_2CO_3).[26] The choice of base plays a vital role in determining the fluorinated linkage of FAVE polymers. The new FAVE polymers formed highly transparent tough films from solution (Figure 2).

As step-growth polymerization progresses, the conversion of trifluorovinyl ether (TFVE) groups was followed by the disappearance of the well-defined ^{19}F NMR AMX pattern (Figure 3A) of the —OCF═CF_2 group at −120 ppm (F_A), −126 ppm (F_M), and −135 ppm (F_X). With the formation of polymer, a broad multiplet splitting pattern for geminal fluorine's (—O—C[F_C]$_2$—) appears at −88 ppm, and lone fluorine (—CF_BH—O—) gives a multiplet near −140 ppm (Figure 3B,C). Employing Cs_2CO_3 as a base exclusively generates polymers **P1′–P2′** bearing hydro-1,-2,2-trifluoroethyl (*W* = —CHF—CF_2—) bridges. However, using sodium hydride as a base, polymers **P1–P2** containing 1,2-difluorovinylene (both *Z*/*E* for —CF═CF—) were

TABLE 1 Selected properties of FAVE polymers **P1–P2** and **P1′–P2′**

		Molecular weight ($\times 10^{-3}$ g/Mol)[b]				5% wt. loss (°C)[d]		Yield at 800°C (%)[e]	
FAVE polymers	**%*W* = CF═CF**[a]	M_n	M_w	M_w/M_n	T_g (°C)[c]	N_2	Air	N_2	Air
P1	1	20	28	1.3	126	285	175	44	0
P1′	0	10	15	1.5	122	324	235	43	0
P2	53	84	237	2.8	120	343	369	21	2
P2′	0	13	22	1.6	129	306	197	42	0

[a] Determined by ^{19}F NMR peak integration.

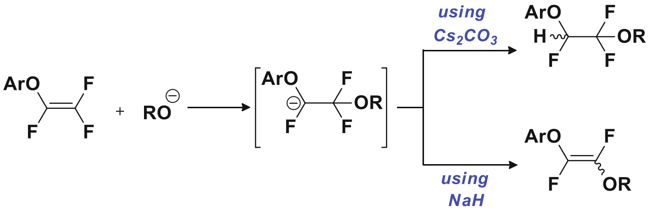
[b] Determined by GPC using THF as a solvent (1 ml/min) at 35°C and polystyrene as a standard.

[c] Determined by DSC (10°C/min in N_2), third heating cycle.

[d] 5% weight losses were obtained by TGA under N_2 or air.

[e] Char yield (at 800°C) obtained by TGA under N_2 or air for **P1–P2** (NaH, base) and **P1′–P2′** (Cs_2CO_3, base).

afforded in addition to the typical presence of the hydroproduct. The ^{19}F NMR spectrum (Figure 3B) reveals the *Z*-isomer (around −119 ppm) and the *E*-isomer (around −125 ppm). The ratio of *Z* and *E*-isomers for polymer **P2** was 2:1, where the overall degree of unsaturation is 53%; whereas for polymer **P1**, *Z*:*E* is 9:1 for only 1% unsaturation. The presence of two electron-withdrawing trifluoromethyl (CF_3) groups during formation of **P2** increases the electrophilicity of TFVE and stabilizes the resulting anionic intermediate during nucleophilic addition/elimination. These effects may increase the rate of polymerization towards relatively higher degree of unsaturation and may account for the higher molecular weight achieved for polymer **P2**. Consistently, the broad PDI of **P2** (Table 1) indicates branching presumably via end-group attack of internal fluoroalkenes.



SCHEME 2 Generalized base selective nucleophilic addition/elimination paths.

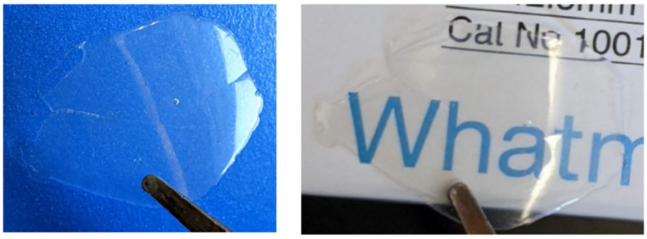


FIGURE 2 Solution (THF) prepared film of FAVE polymer **P2**

As isosorbide is a 'head-tail' monomer with exo and endo hydroxyl groups with unequal reactivity,[18] the resulting FAVE polymers of isosorbide exhibit complicated splitting patterns due to the geminal fluorine atoms (F_c), which are typically shown as an AB pattern with traditional FAVE polymers from symmetric monomers. The base-mediated nucleophilic addition/elimination polymerization of isosorbide affords both head-to-head and head-to-tail addition. Unlike **P2** with a higher degree of alkene content, the asymmetric environment due to the presence of enantiotopic fluorine F_B adjacent to diastereotopic F_c in polymer **P2′**, in addition to the

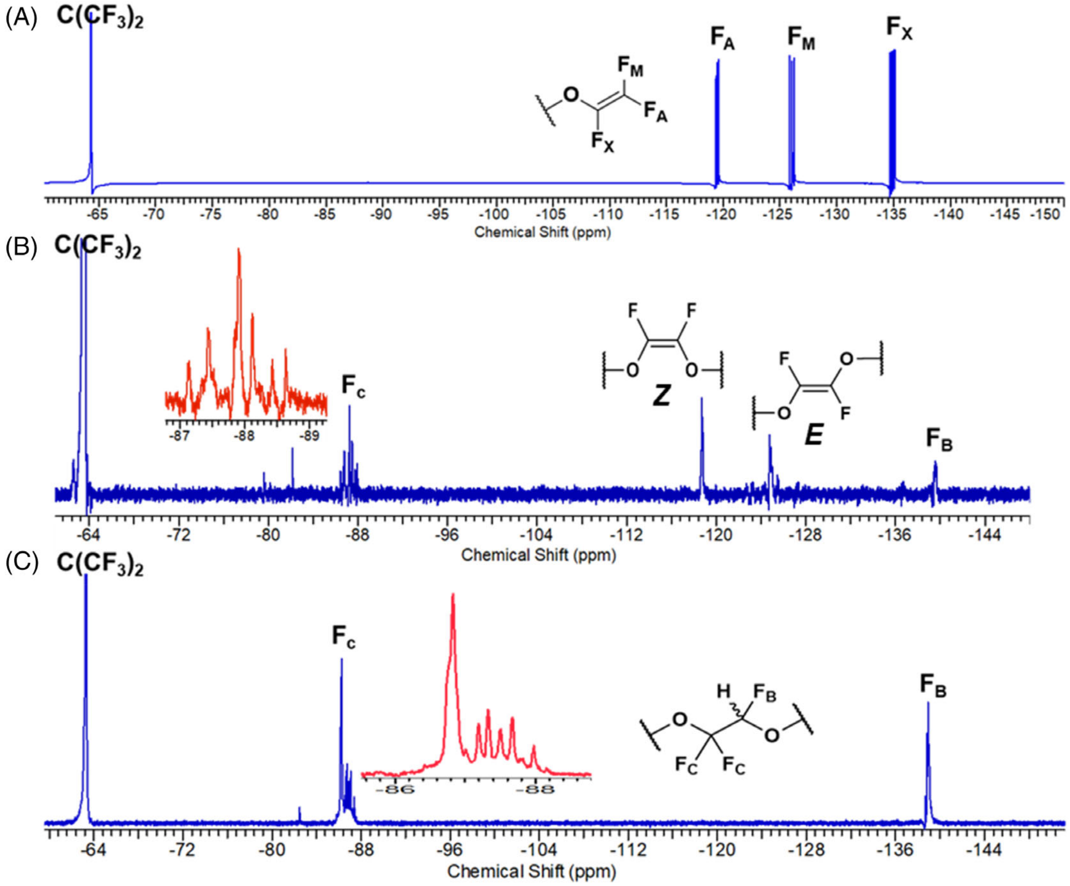


FIGURE 3 ^{19}F NMR (in CD_2Cl_2) spectra of 6F-*bis*-TFVE monomer (A), polymer **P2** (B), and polymer **P2′** (C)

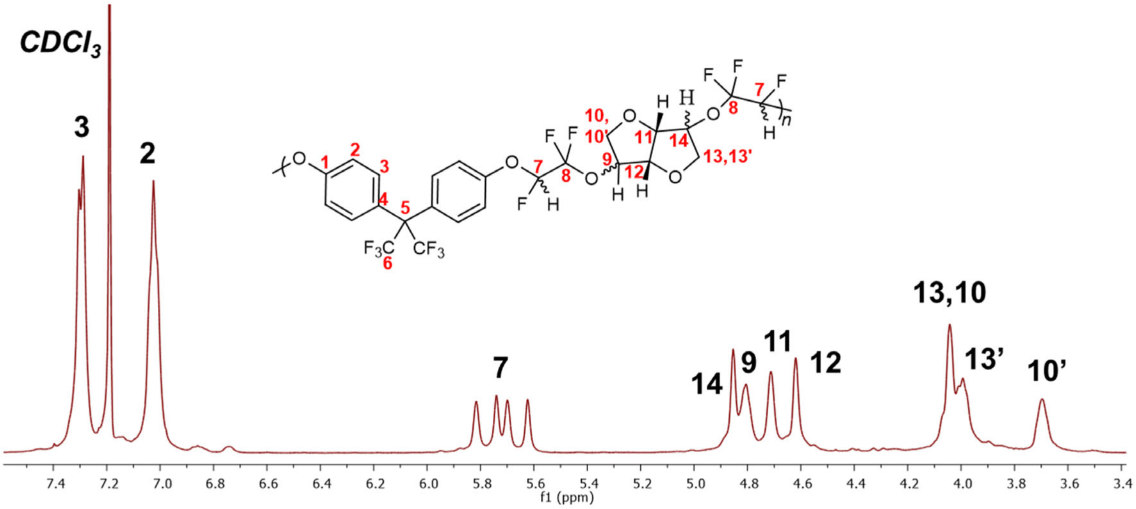


FIGURE 4 ^{1}H NMR spectrum in $CDCl_3$ of FAVE polymer **P2′**

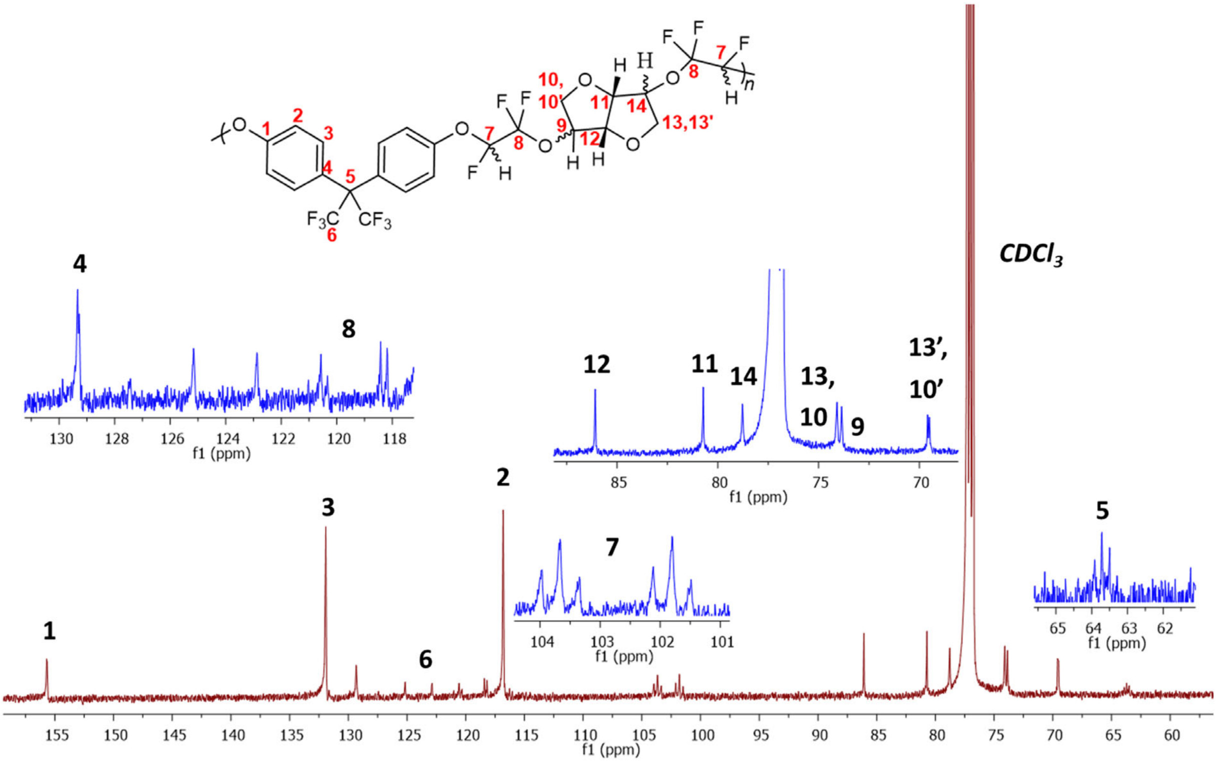


FIGURE 5 ^{13}C NMR spectrum in $CDCl_3$ of polymer **P2′** with inset expanded regions

regioselectivity generated by the hydroxyl reactivity differences, may produce such complicated fluorine splitting patterns.

Characteristic properties of the renewable FAVE polymers are shown in Table 1. The number average molecular weight (M_n) ranged from 10 to 84 kDa with polydispersitites ranging from 1.3 to 2.8. The choice of the base and *bis*-TFVE monomer played a key role in the resulting molecular weight distribution. The polymers obtained using Cs_2CO_3 as a base **P1′** and **P2′** exhibited relatively low-molecular weight when compared to polymers **P1** and **P2** (obtained using NaH base). Among all FAVE polymers, only polymer **P2** displayed exceptional molecular weight (84 kDa) with PDI 2.8.

The ^{1}H NMR spectra of fluorinated arylene vinylene ether (FAVE) polymer **P2′** is shown in Figure 4. The presence of the saturated fluorocarbon linkage ($CHFCF_2$, H7) is observed as a characteristic dd splitting pattern

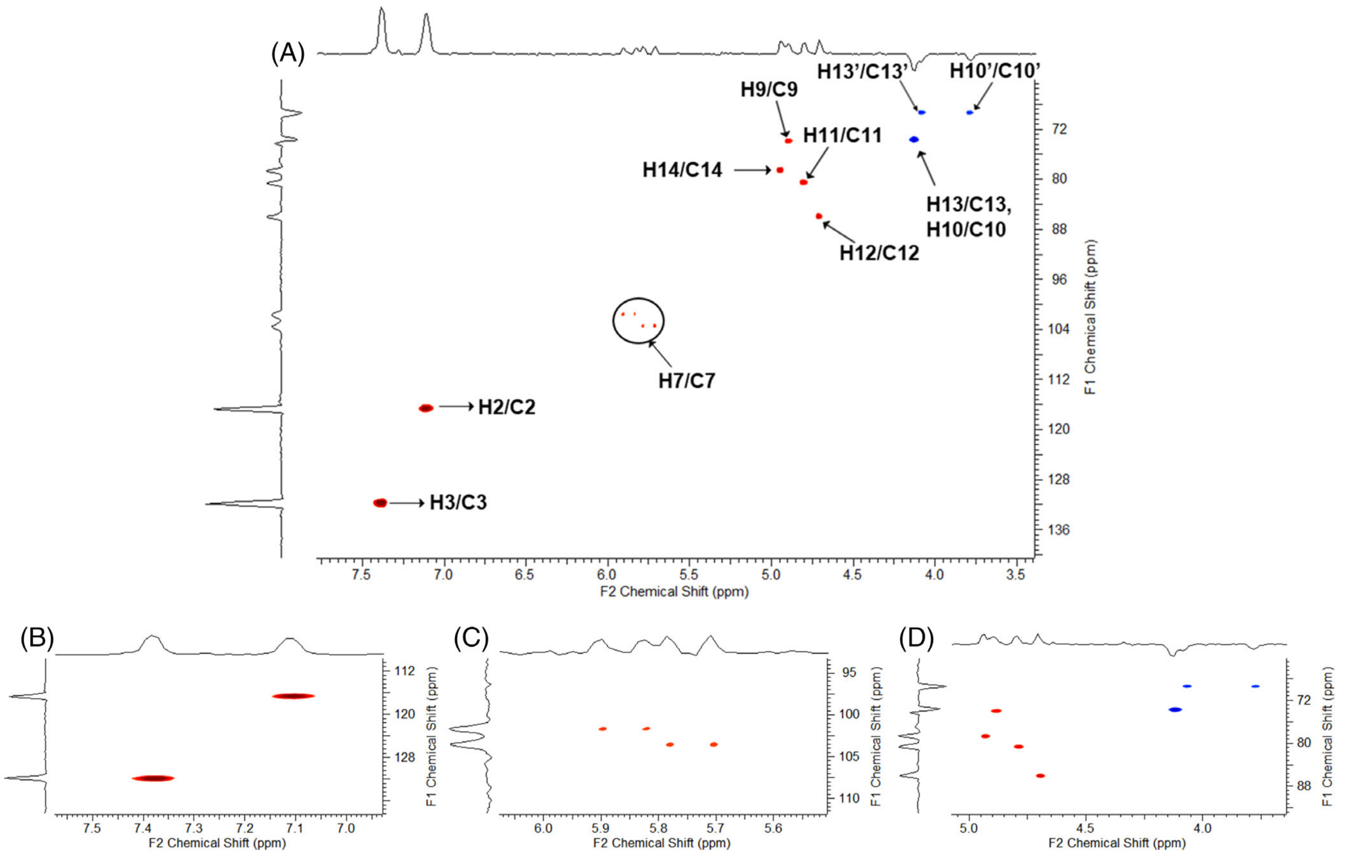


FIGURE 6 Heteronuclear single quantum coherence (HSQC) of polymer **P2′**: Complete 2D spectra (A), expanded correlation of aromatic protons (B), expanded correlation of H7 (C), and expanded correlation of aliphatic isosorbide signals (D)

centered at 5.79 ppm with coupling constants, $J = 58.5$ and 37.8 Hz. Additionally, after the nucleophilic addition/elimination reaction, the proton signals ranging from 3.7 to 5 ppm represent both, presumably random, head-to-head and head-to-tail isosorbide enchainment. 2D NMR experiments further confirmed the assignment of the proton and carbon signals in the spectra.

Figure 5 represents the ^{13}C NMR spectra of FAVE polymer **P2′**. The two aromatic CH signals appear at ~132 and 116 ppm; however, the two aromatic quaternary C signals appear at 155 and 129 ppm. Carbon signals for the isosorbide unit in the polymer are observed between 60 and 90 ppm. The presence of fluorine in **P2′** was evident from the C—F geminal and vicinal splitting pattern of ^{13}C NMR signals found from 101 to 104 ppm as a characteristic doublet of triplets (dt) with coupling constants, $J = 235.0$ and 39.5 Hz, and a poorly resolved triplet of doublets (td, shown as C8 in Figure 5).

Figure 6 displays the heteronuclear single quantum coherence (HSQC) spectra of FAVE polymer **P2′**. The HSQC correlated spectrum shows CH_2 signals in blue and CH/CH_3 peaks in red and in the opposite phase. Figure 6B illustrates the expanded aromatic region correlation from HSQC experiments. Identification of proton H7 on carbon C7 is revealed as a dd due to splitting by three neighboring fluorine atoms. This dd signal is coupled with a doublet of triplets (dt) pattern, as shown in the Figure 6C. Thus, the proton signals around 3.7 and 4.1 are H10 and H12. The two blue peaks corresponding to a single carbon correlate with non-equivalent methylene protons H10'/H13' whereas H10/H13 correlate as equivalent (Figure 6D). TOCSY (Figure S4) played an additional role in understanding the proton correlations in the polymer. For example, H7 in the fluorinated linkage is not correlated with any protons as expected. HMBC (Figure S5) gave correlation between carbons and protons that are separated by two bonds (via the ether linkage) such that carbon C1 correlated with the aromatic protons as well as H7.

Thermal studies of the polymers **P1–P2** and **P1′–P2′** were examined by DSC and TGA. Figure 7 shows the glass transition temperatures (T_g) of the synthesized renewable FAVE polymers measured by DSC. The T_g ranged from 120 to 130°C, indicating no significant difference upon changing the bisphenol spacer group or the degree of unsaturation in the fluorinated linkage (Table 1). FAVE polymers **P1** and **P2**, obtained using sodium hydride as a base, contains unsaturated

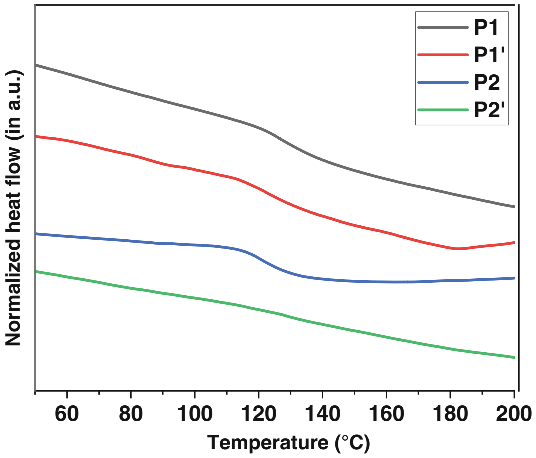


FIGURE 7 Third DSC heating cycle performed at 10°C/min under nitrogen for renewable semi-fluorinated polymers **P1–P2** and **P1′–P2′**

fluorocarbon (—CF═CF—) linkages with the ability to thermally crosslink. Further, the DSC analysis of FAVE polymer **P2** showed a slightly increasing value to a maximum T_g of 120°C after third heating cycle to 400°C at 10°C/min in nitrogen (Figure S6, top). With subsequent reheating to the fourth cycle, a clear T_g was not observed, indicating thermal crosslinking of fluoroalkenes (53% in **P2**, see Table 1) has occurred producing an insoluble network. Similarly, for polymer **P1** (Figure S7, top), a change in T_g was observed from 126 to 148°C (fourth cycle), which also produced an insoluble network. As expected, polymers **P1′** and **P2′** (no observed unsaturation, Table 1) gave soluble polymers with reproducible T_g values after multiple cycles and no indication of crosslinking. Such crosslinking ability of fluoropolymers can be used for variety of applications especially coatings and specialty elastomers. Further, the onset of crosslinking for both polymers **P1** and **P2** was observed around 280°C. Thus, when heating these unsaturated FAVE polymers above 280°C, an exothermic event is measured (Figures S6 and S7) representing thermal crosslinking of internal fluoroolefin groups present.

The polymers **P1–P2** and **P1′–P2′** demonstrated average thermal stabilities (T at 5% wt. loss) both ranged from 285 to 343°C under nitrogen and 175 to 369°C in air (Figure S8, Table 1). All polymers showed two distinct thermal degradation events that may be attributed to initial ring cleavage of strained bicyclic isosorbide moieties, followed by stronger fluorocarbon and aromatic bond cleavage. The dramatically lower char yield for FAVE polymer **P2** may suggest that olefin content (highest in **P2** at 53%, Table 1) may be key to increasing the rate of degradation by mechanisms in preference to others available to the saturated fluorocarbon linkage.

4 | CONCLUSION

Facile and efficient base-mediated nucleophilic addition/elimination step-growth polymerization produced fluorinated arylene vinylene ether (FAVE) polymers containing renewable isosorbide units (23–31 wt.%). Previously limited to using bisphenols or primary diol monomers, isosorbide enchainment demonstrates for the first time that secondary (cyclic) diol monomers can be included to produce FAVE polymers. Choice of base played an important role in generating the unsaturated or saturated fluorocarbon linkages in the polymer. The new FAVE polymers exhibited reasonably high-molecular weight and formed tough transparent films from solution in common solvents. Moderate glass transition temperatures (120–130°C) were observed, and the unsaturated polymers exhibited thermal crosslinking capability. In general, semi-fluorinated FAVE polymers containing isosorbide units and reactive fluoroalkenes capable of post-polymerization functionalization may have potential for applications in specialty coatings, packaging, or elastomer technology.

AUTHOR CONTRIBUTIONS

Ketki Eknath Shelar: Conceptualization (lead); data curation (lead); formal analysis (lead); methodology (lead); writing – original draft (lead); writing – review and editing (equal). **Karl M. Mukeba:** Data curation (supporting); methodology (supporting); writing – review and editing (supporting). **Kelly Mills:** Data curation (supporting); writing – review and editing (supporting). **Dennis W. Smith Jr.:** Funding acquisition (lead); project administration (equal); supervision (lead); writing – review and editing (equal).

ACKNOWLEDGMENTS

The authors gratefully acknowledge Mississippi State University Department of Chemistry and the NSF-REU Site: Food, Energy, and Water Security grant no. 1852527 in part for financial support. Generous donation of intermediates and TFVE monomers by Tetramer Technologies, LLC (Pendleton, SC) is greatly appreciated. We also thank Prof. Charles U. Pittman, Jr. for helpful advice.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

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How to cite this article: K. E. Shelar, K. M. Mukeba, K. Mills, D. W. Smith Jr., *J. Polym. Sci.* **2022**, *60*(16), 2500. https://doi.org/10.1002/pol.20220161