Facile preparation of fluorovinylene aryl ether telechelic polymers with dual functionality for thermal chain extension and tandem crosslinking†

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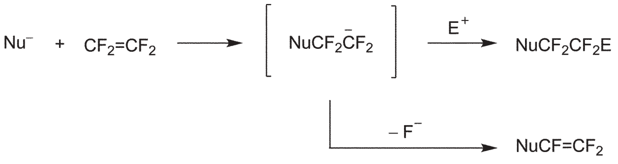
New fluorovinylene aromatic ether polymers, possessing dual reactivity, have been successfully prepared *via* the step-growth polymerization of commercial bis(trifluorovinyl) aromatic ethers and bisphenols.

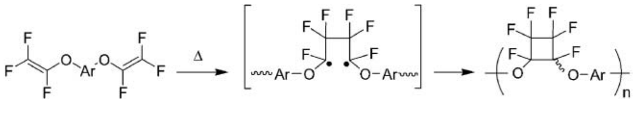
Nucleophilic addition to fluorinated alkenes is widely known[1] (Scheme 1) and is of major commercial importance to the fluoroelastomer[2,3] industry, where, for example, phenols and amines are used to crosslink unsaturated fluoropolymers. Step-growth polymer chemistry can also be used to access aliphatic perfluorinated polyethers exhibiting low surface energy, exceptional thermal and chemical resistance, and excellent electrical insulating properties.[4,5]

However, despite these advances, most fluoropolymers are prepared by radical-mediated chain polymerization, exhibit a high degree of crystallinity and require labor-intensive processing conditions, leading to costly effluent waste management.[3]

Here we report the facile preparation of fluorovinylene aromatic ether polymers *via* the step-growth polymerization of commercial bis(trifluorovinyl) aromatic ethers with common bisphenols. The resulting polymers possess dual functionality and are telechelic in nature, with intact trifluorovinyl aromatic ether end groups and well defined difluorodioxyvinylene enchainment, produced by the addition of bisphenoxide and the subsequent elimination of fluoride. Dual fluoroolefin functionality of this type provides tandem thermally-initiated chain extension and crosslinking without additives or initiators. Chain extension occurs when trifluorovinyl aromatic ether end groups thermally polymerize *via* [2 + 2] cyclodimerization to form perfluorocyclobutyl (PFCB) aryl ether linkages near 150–210 °C (Scheme 2), followed by crosslinking *via* the internal fluorooxyvinylene groups near 250 °C.



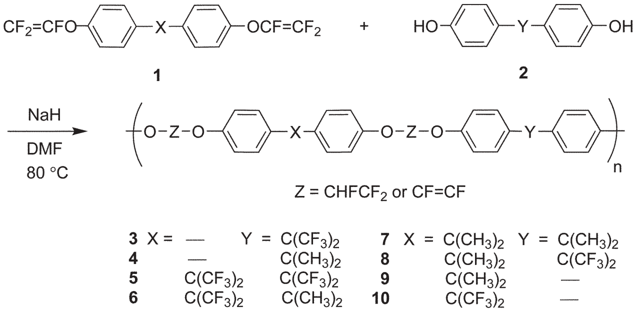
Scheme 1 Nucleophilic additions to substituted trifluoroethylene.



Scheme 2 Thermal PFCB aryl ether chain extension polymerization.

Perfluorocyclobutyl aryl ether polymers have demonstrated much success as processable and amorphous fluoropolymers,[6] with particular emphasis on high performance optical applications.[7] Fluorovinylene aromatic ether polymers and the general strategy for the step-growth polymerization of bisphenols and bis(trifluorovinyl) aromatic ether monomers were not known previously.

Our investigation focused on employing the step-growth polymerization of commercially available bis(trifluorovinyl) aryl ethers **1** with common bisphenols **2** in a 1 : 1 molar ratio, affording transparent, film-forming polymers **3–10**, as shown in Scheme 3. Selected polymer properties are presented in Table 1. The



Scheme 3 Preparation of polymers **3–10**.

Table 1 Selected properties of polymers **3–10**

Entry	Z ratio $CHFCF_2$/ CF=CF	$M_n \times 10^{-3}$ GPC[a] (NMR)[b]	M_w/M_n	T_g/°C[c]	T_d/°C N_2 (air)[d]
3	1.0	12.1	2.0	88	324, 554 (551)
4a	1.3	23.4 (15.0)	1.4	95	319, 524 (561)
4b	4.9[e]	11.8	1.7	34	336, 513 (632)
5	2.8	15.8	1.8	102	370, 521 (534)
6	0.91	(11.8)	—	122	302, 543 (566)
7	0.25	(14.3)	—	90	321, 534 (512)
8	1.1	(35.5)	—	44	343, 439 (565)
9	1.4	(13.6)	—	99	313, 523 (436)
10	4.0	(15.0)	—	112	310, 528 (486)

[a] GPC in $CHCl_3$ using polystyrene standards. [b] Determined by ^{19}F NMR. [c] DSC (10 °C min^{-1}) in nitrogen, second heating. [d] TGA onset at 10 °C min^{-1}. [e] Cs_2CO_3 used as base (50 mol%).

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optimized conditions, to date, involve generation of the bisphenoxide sodium salt of **2** using NaH in DMF, followed by stoichiometric addition of **1** at 80 °C for 24 h. This method produced polymers possessing both internal fluoroolefins (Z = –CF=CF–) from the elimination of fluoride and hydrofluoro ethyl groups (Z = $-CHFCF_2-$) after aqueous precipitation.[8]

For the internal fluoroolefins, a 1 : 1 *cis* : *trans* isomer ratio was observed by ^{19}F NMR in all cases. This observation is consistent with the phenol additions to perfluorovinyl alkyl ethers studied by Feiring.[9] The degree of unsaturation can also be controlled by substitution of the spacer group in **1** or **2**. As shown in Table 1, substitution with electron withdrawing groups (for example, X or Y = $-C(CF_3)_2-$) retards the degree of unsaturation.

Using Cs_2CO_3 (50 mol%) to prepare polymer **4b**, 80% hydrofluorination was achieved. This result is consistent with the observation that the trifluoroethylene anion intermediate (Z = $-CF_2CF^{-}-$) is protonated and regenerates the carbonate base.[9]

Differential scanning calorimetry (DSC) studies on **3–10** demonstrate a broad range of glass transition temperatures (T_g) at 34–122 °C. For all polymers studied, crosslinking of the internal fluoroolefin (Z = –CF=CF–) gave exotherm onsets at 220–300 °C. Fig. 1 shows the DSC data for polymer **4a** before and after heating to 300 °C in nitrogen. A clear T_g was observed at 95 °C for the amorphous thermoplastic, whereafter crosslinking the polymer revealed no T_g, indicating a densely crosslinked network.

Thermogravimetric analysis (TGA) of polymers **3–10** exhibited two decomposition temperatures (T_d) in nitrogen, whereas only a single T_d was observed in air. For example, Fig. 2 shows the two distinct decomposition events of polymer **4a**, and is representative of all the polymers studied. No more than 5% mass loss was observed after the first T_d in nitrogen. A single T_d was observed in air, and may be the result of oxidation of the internal fluoroolefin. This would be consistent with earlier work, which reported that fluorinated vinyl ethers oxidize in air at elevated temperatures and undergo stabilizing skeletal rearrangement before decomposition.[10] Overall char yields ranged from 30–40% at 900 °C in nitrogen, producing glass-like solids.

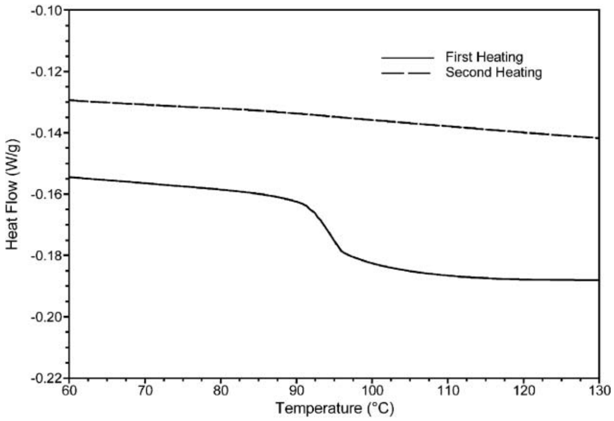


Fig. 1 DSC thermogram of polymer **4a**.

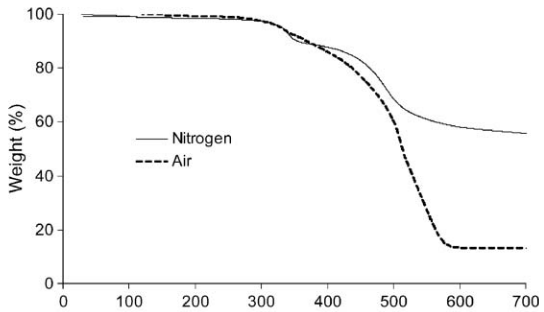
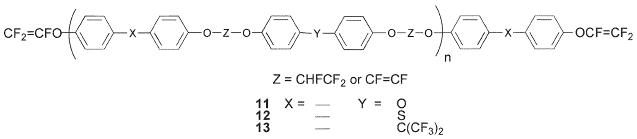


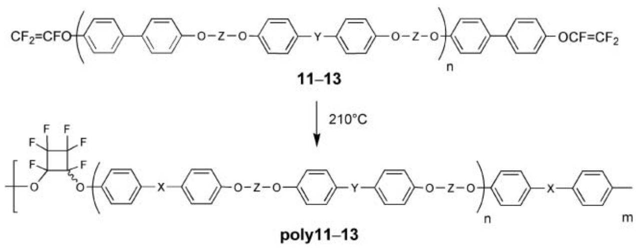
Fig. 2 Thermal decomposition of polymer **4a** in nitrogen and air.

Attempts to radically polymerize the internal difluorodioxyvinylene groups with hν or thermal initiators, such as AIBN and benzoyl peroxide, failed to induce chain growth. As previously reported, even trifluorovinyl aryl ethers do not undergo radical-initiated polymerizations under such conditions.[11]

Telechelic polymers **11–13** were prepared, as shown in Scheme 4, using a similar methodology to the preparation of polymers **3–10**. Using a slight modification, the addition of excess sodium salt of bisphenol **2** to bis(trifluorovinyl) aryl ethers **1** produced end-capped telechelic polymers. Telechelomers **11–13** contained up to 92% fluoroolefin content, previously unachieved with polymers **3–10**. While the molecular weight was limited for the telechelics, this strategy provided convenient access to processable PFCB aryl ether polymers *via* thermal chain extension, without crosslinking, as illustrated in Scheme 5. Selected properties of the telechelomers and their respective PFCB chain extended polymers are shown in Table 2.



Scheme 4 Trifluorovinyl ether end-capped bisphenol telechelomers **11–13**.



Scheme 5 Thermal PFCB chain extension polymerization of **11–13**.

Table 2 Selected properties of chain extended telechelomers **11–13**

Entry	Z = $CHFCF_2$/ CF=CF	$M_n \times 10^{-3}$ GPC[a] (NMR)[b]	M_w/M_n	T_g/°C[c]	T_d/°C N_2 (air)[d]
11	0.67	1.3 (2.5), 6.3[e]	1.6, 2.2[e]	10, 70[e]	283, 534 (262, 525)
12	0.24	1.2 (2.0), 9.8[e]	1.6, 3.3[e]	27, 57[e]	310, 550 (304, 600)
13	0.08	1.7 (4.1), 13.9[e]	1.4, 5.3[e]	12, 83[e]	340, 543 (560)

[a] GPC in $CHCl_3$ using polystyrene standards. [b] Determined by ^{19}F NMR end group analysis. [c] DSC (10 °C min^{-1}) in nitrogen, second heating. [d] TGA onset at 10 °C min^{-1} of chain extended polymers. [e] After chain extension to PFCB polymers (210 °C, 1 h).

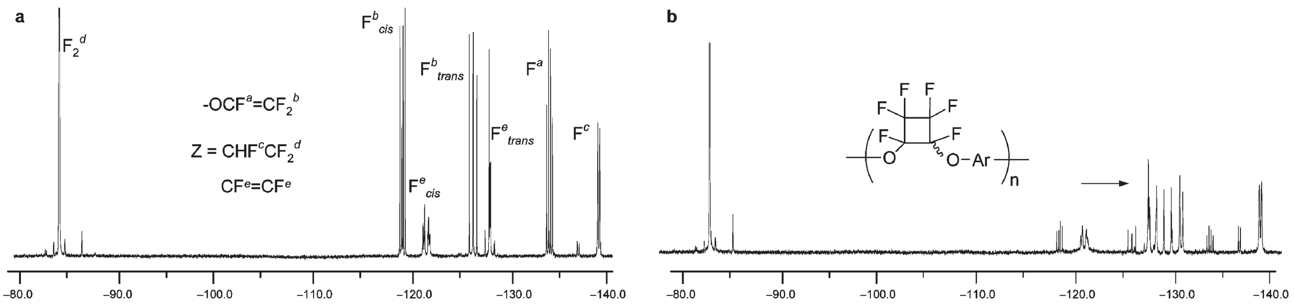


Fig. 3 ^{19}F NMR spectra of (a) telechelomer **11** and (b) chain extended PFCB aryl ether polymer (**poly11**) (b).

Chain extension of telechelomers **11–13** can be thermally controlled to initially induce step-growth trifluorovinyl aryl ether cyclopolymerization at 210 °C (Scheme 5), producing linear PFCB polymers (**poly11–13**). Further heating to 225 °C induced crosslinking of the internal fluoroolefin groups.[12] The network polymers formed from these heat treatments were insoluble materials with no observable T_g below 350 °C.

The controlled thermal chain extension approach is exemplified using **11**, which was subjected to bulk thermal polymerization conditions at 210 °C for 1 h. The PFCB aryl ether polymerization produced a transparent, film-forming polymer of $M_n = 6250$ and a polydispersity of 2.2 (M_w/M_n) by GPC. In this case, the internal perfluoroolefin moieties were unaffected, as evidenced by comparing peak integrations using ^{19}F NMR (Fig. 3). It is also important to note that the hydrofluoroethylene groups (–CHFCF$_2$–) do not undergo thermal dehydrofluorination under these conditions.

In summary, we have developed the first step-growth polymerization of bisphenols to bis(trifluorovinyl) aryl ethers to produce a new class of fluoropolymers from commercial feedstocks. The polymers possess dual functionality, which enables thermal chain extension and tandem crosslinking, affording network polymers without the aid of curing agents. These amorphous fluoropolymers may find application as crosslinking additives for fluoroelastomers, as well as melt- or solution-processable resins for other thermosetting applications.

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Notes and references

1 R. D. Chambers, in *Synthetic Fluorine Chemistry*, ed. G. A. Olah and G. K. Surya Prakash, Wiley & Sons, New York, 1992, pp. 359–380.
2 B. Ameduri, B. Boutevin and G. Kostov, *Prog. Polym. Sci.*, 2001, **26**, 105.
3 J. G. Drobny, *Technology of Fluoropolymers*, CRC Press LLC: Boca Raton, 2001.
4 M.-H. Hung, W. B. Farnam, A. E. Feiring and S. Rozen, *J. Am. Chem. Soc.*, 1993, **115**, 8954.
5 Z. Y. Yang, A. E. Feiring and B. E. Smart, *J. Am. Chem. Soc.*, 1994, **116**, 4135.
6 (*a*) D. A. Babb, B. R. Ezzell, K. S. Clement, W. F. Richey and A. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 3465; (*b*) B. Spraul, S. Suresh, J. Jin and D. W. Smith, Jr., *J. Am. Chem. Soc.*, 2006, **128**, 7055 and references therein.
7 (*a*) D. W. Smith, Jr., S. Chen, S. Kumar, J. Ballato, H. Shah, C. Topping and S. Foulger, *Adv. Mater.*, 2002, **14**, 1585; (*b*) J. Ghim, D.-S. Lee, B. G. Shin, D. Vak, D. K. Yi, M.-J. Kim, H.-S. Shim, J. J. Kim and D.-Y. Kim, *Macromolecules*, 2004, **37**, 5724; (*c*) B. K. Spraul, S. Suresh, S. Glaser, D. Perahia, J. Ballato and D. W. Smith, Jr., *J. Am. Chem. Soc.*, 2004, **126**, 12772; (*d*) Y.-H. Niu, Y.-L. Tung, Y. Chi, C.-F. Shu, J. H. Kim, B. Chen, J. Luo, A. J. Carty and A. K.-Y. Jen, *Chem. Mater.*, 2005, **17**, 3532.
8 When Z = CHFCF$_2$, the unit is directional in accordance with the order of the diaryl spacer group (X and Y). Therefore, the order should represent –Y–Ar–O–CHFCF$_2$–O–Ar–X– as a repeat unit.
9 A. E. Feiring and E. R. Wonchoba, *J. Org. Chem.*, 1992, **57**, 701.
10 R. S. Corley, J. Lal and M. W. Kane, *J. Am. Chem. Soc.*, 1956, **78**, 3489.
11 W. J. Pummer and L. A. Wall, *SPE Trans.*, 1963, **3**, 220.
12 Model studies are under way to investigate the mechanism and kinetic behavior of thermal crosslinking.