ELSEVIER

Journal of Fluorine Chemistry 104 (2000) 109–117

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Perfluorocyclobutane (PFCB) polyaryl ethers: versatile coatings materials

Dennis W. Smith Jr.[a,*], David A. Babb[b], Hiren V. Shah[a],
Adrienne Hoeglund[a], R. Traiphol[a], Dvora Perahia[a],
Harold W. Boone[b], Charles Langhoff[b], Mike Radler[b]

[a]*Department of Chemistry, Clemson University, Clemson, SC 29634, USA*
[b]*Corporate Research, The Dow Chemical Company, Midland, MI, USA*

Abstract

The cyclopolymerization of aromatic trifluorovinyl ether (TFVE) monomers offers a versatile route to a unique class of linear and network fluoropolymers containing the perfluorocyclobutyl (PFCB) linkage. Polymerization proceeds by a thermal — radical mediated — step-growth mechanism and provides well-defined polymers containing known fluoroolefin end groups. PFCB polymers combine the engineering thermoplastic nature of polyaryl ethers with fluorocarbon segments and exhibit excellent processability, optical transparency, high temperature performance, and low dielectric constants. An intermediate strategy utilizing Grignard and aryllithium reagents has been developed which offers access to a wide variety of hybrid materials amenable to coatings applications. Liquid crystalline examples have recently been achieved in addition to tailoring optical properties by co-polymerization.

Keywords: Cyclopolymerization; Perflurocyclobutane polymers; Trifluorovinyl ethers; Raman spectrocopy

1. Introduction

Many practical coatings applications of highly crystalline or high melt viscosity perfluorinated materials, such as TeflonTM are often limited due to prohibitive processing costs [1–3]. Incorporation of partially fluorinated segments or substituents, however, yield polymers with low dielectric constant, moisture resistance, low surface energy, thermal and thermal-oxidative stability, and chemical resistance without sacrificing — and frequently improving — processability [1–3]. Our efforts have focused on the development of a unique class of semi-fluorinated polymers which utilize the thermal cyclopolymerization of aryl trifluorovinyl ethers (TFVEs) from which a variety of thermoplastic and thermosetting polymers containing the perfluorocyclobutane (PFCB) aromatic ether linkage have been obtained (Scheme 1) [4–14]. The combination of processability and performance provided by PFCB polymers makes them natural candidates for applications, such as high performance structural coatings, interlayer dielectrics, circuit board laminates, dielectric wave guides, optical cladding layers, and coatings for space applications [15–20].

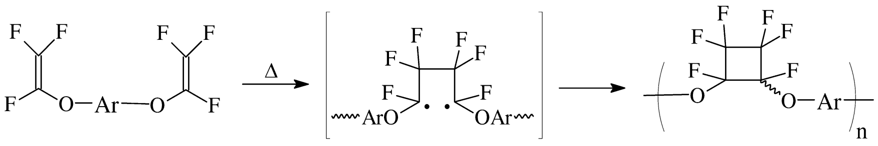
The cyclodimerization of TFVEs is activated thermally and is favored for fluoroolefins due to an increased double-bond strain, a lower π-bond energy, and the strength of the resulting fluorinated C–C single bond cycloadducts in contrast to hydrocarbon analogs [21]. As generalized in Scheme 1, predominant head-to-head cycloaddition proceeds to form the more stable diradical intermediate followed by rapid ring closure giving essentially an equal mixture of *cis*- and *trans*-1,2-disubstituted PFCB linkages. Both direct measurements on polymers [4] and model studies [8] have consistently revealed an equal isomeric distribution in PFCB polymers.

The PFCB approach has been to combine flexible, yet thermally robust, aromatic ethers with fluorocarbon linkages, thereby providing fluoropolymers which are easily processed from solution or the melt. High molecular weight PFCB thermoplastic polymers or solution advanced thermosetting resins can be spin coated and cured giving films which exhibit high glass transition temperature's (T_g), good thermal stability, optical clarity, and isotropic dielectric constants around 2.3 at 1 MHz. The step growth addition type polymer chemistry which proceeds to form PFCB polymers is thermally activated, does not require catalysts or initiators, and does not produce condensation products during polymerization or final cure. Cycloaddition polymer-

---

[*] Corresponding author. Tel.: +1-8646565020.
E-mail address: dwsmith@clemson.edu (D.W. Smith Jr.)

0022-1139/00/$ – see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0022-1139(00)00233-5



Scheme 1. Cyclopolymerization of Trifluorovinyl Ether monomers.

ization of this type results in well defined linear or network polymers containing known trifluorovinyl aromatic terminal groups at any stage of polymerization [4].

2. Results and discussion

2.1. Traditional PFCB coatings materials

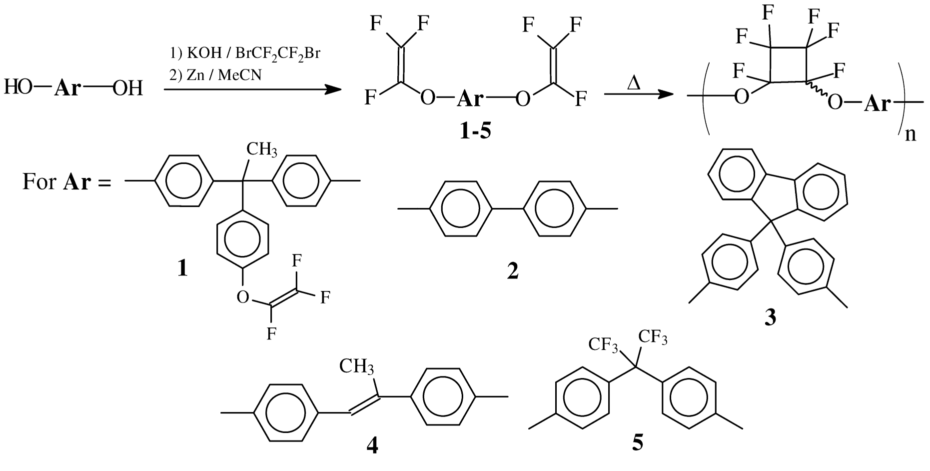
Traditional TFVE monomers are prepared in two steps from commercially available phenolic precursors via fluoroalkylation with $BrCF_2CF_2Br$ followed by Zn mediated elimination (Scheme 2) [10–11]. The trifunctional monomer prepared from tris(hydroxyphenyl)ethane (**1**) has, thus, far been the primary focus for PFCB technology targeted for coatings applications. However, other monomers and polymers containing bisphenylfluorene, [10] phosphine and phosphine oxide [6,10], triphenyl benzene [11], siloxane [4,12–13], and phosphazene [14] linkages have been reported. Scheme 2 illustrates the structural versatility of selected TFVE monomers prepared from phenolic precursors.

The polymerization reaction of trifunctional monomer **1** forms a branched oligomer containing unreacted TFVE terminal groups. As predicted for trifunctional monomers undergoing step growth polymerization, the polydispersity of the soluble oligomers grows steadily with molecular weight prior to gelation near 50% conversion. Trifluorovinyl aryl ether monomers undergo spontaneous exothermic cyclopolymerization at relatively mild (>130°C) temperatures due to a weak and strained C=C π-bond. The cyclodimerization of tetrafluoroethylene was reported to proceed with a $\Delta H = -50$ kcal/mol due to this unique fluoroolefin reactivity [22]. For TFVE monomers, exothermic polymerization reaches a measurable rate (DSC at 10°C/min) near 140°C and polymerizations are typically carried out at temperatures between 150–210°C [5].

The classical step growth kinetics by which PFCB polymers are formed allows for easy control of parameters important to coating technology in general. Monomer can be solution advanced at 150°C in typical solvents to a precisely controlled viscosity, molecular weight, and polydispersity [5–6]. The pre-polymer solution formed can be spin-coated giving defect free films. Final cure can then be achieved by post baking under nitrogen or air at temperatures ranging from 235–325°C for several hours depending on the application.

Polymerization kinetics for monomer **1** has recently been studied in detail by Raman spectroscopy [5]. This technique is well suited for fluoroolefin conversion due to the enhanced signal of fluoroolefins and the possibility of fast and non-destructive measurement. Fig. 1 compares the Raman spectra of pure monomer **1**, an oligomeric film spin coated from mesitylene solution on silicon, and the fully cured film (3–6 μm in thickness).

Clearly, the Raman signal representing the perfluorinated C=C stretching at 1831 cm^{-1} can be used to monitor the concentration of reactive groups remaining during initial polymerization as well as final cure on the substrate. The 1831 cm^{-1} peak was normalized using the phenyl ring vibration at 1605 cm^{-1} as an internal standard. The spectrum of the fully cured material (300°C, 50 h) in Fig. 1 shows that the 1831 cm^{-1} band will disappear after long cure times at high temperature demonstrating that complete



Scheme 2. PFCB polymers prepared from bis-phenols.

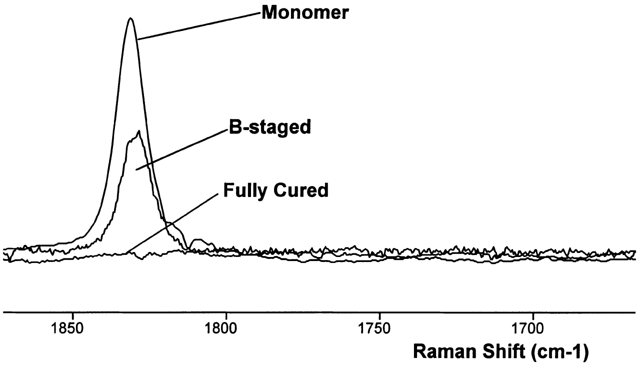


Fig. 1. Trifluorovinyl consumption in monomer **1** by Raman spectroscopy.

Table 1
Selected properties of PFCB thermoset polymer from monomer **1**

Tensile strength (MPa)	66.0±1.4
Tensile modulus (MPa)	2.270±79
Flexural strength (MPa)	74±12
Flexural modulus (MPa)	2.320±13
% Elongation (break)	4.1
T_g (DMA)	380°C
Dielectric constant (10 kHz)	2.35
Dissipation factor (10 kHz)	0.0004
% Water absorption (24 h)	0.021
Refractive index (800 nm)	1.495

conversions can be determined by the Raman technique. This allows for the subtle effect of cure conversion on performance to be revealed. For example, in thin film applications, T_g will change during processing depending on the degree of cure, thereby affecting other critical interrelated parameters, such as modulus, toughness, stress, and adhesion.

The extent of cure versus time is plotted in Fig. 2 for cure temperatures of 130, 150, 170, 190, and 210°C. The half-life varies from ~450 min to less than 10 min at these temperatures. From this data, the Arrhenius relationship of $-\ln(k)$ versus $1/T$ gave an activation energy of 103 kJ/mol or 24.6 kcal/mol. This value agrees well with activation energies determined by other methods, such as DSC, GPC and NMR.

The thermal and thermal oxidative stability of PFCB polymers, as well as the degradation mechanism and zeroth order kinetic analysis has been reported in detail [9,6]. Using dynamic thermogravimetric (TGA) analysis at 10°C/min in nitrogen, the fully cured polymer shown in Fig. 2 retains 100% of its weight to >470°C after which catastrophic degradation ensues (T_{onset}=475°C). However, a more practical measure of thermal stability is obtained by isothermal TGA analysis where the same polymer exhibits a weight loss of <0.05%/h in nitrogen and 0.7%/h in air at 350°C. PFCB polymers, in general, thermally degrade by homolytic cleavage at the cyclobutyl ether linkage forming hexafluorocyclobutene [9]. Table 1 gives additional selected properties for the thermoset polymer prepared from monomer **1** [10].

The PFCB films obtained exhibit exceptional planarization of topographical features, and have also demonstrated the ability to smooth substrates, such as color pixels for flat panel displays [20]. In addition, the pre-polymer has been shown to planarize Canasite glass ceramic substrates used in magnetic data storage devices [15]. PFCB polymers have also been used as an electronic buffer layer in the preparation of multilayer Mach–Zender intensity modulator waveguiding devices [15–20].

2.2. The intermediate strategy

The traditional synthesis of TFVE monomers relied on fluoroalkylation followed by zinc mediated elimination of phenolic precursors (Scheme 2). Since cost and availability are limiting factors to any technology, we undertook a study to develop methods to deliver the trifluorovinyl aryl ether group to a wide variety substrates directly from reasonably accessable, and low cost, precursors. We chose simple

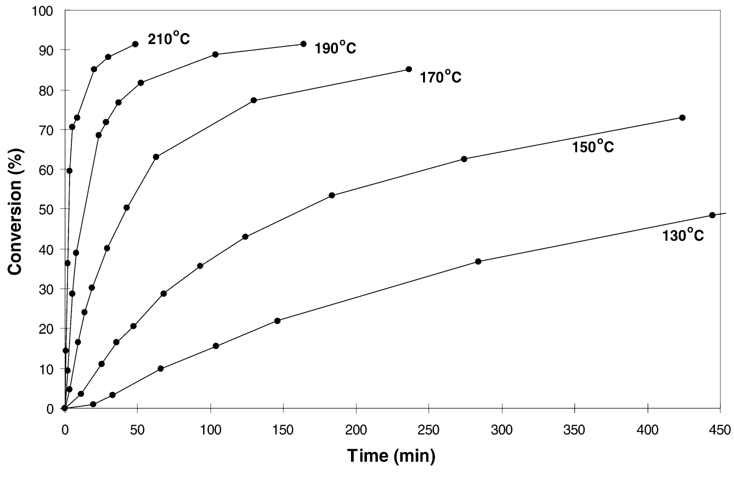
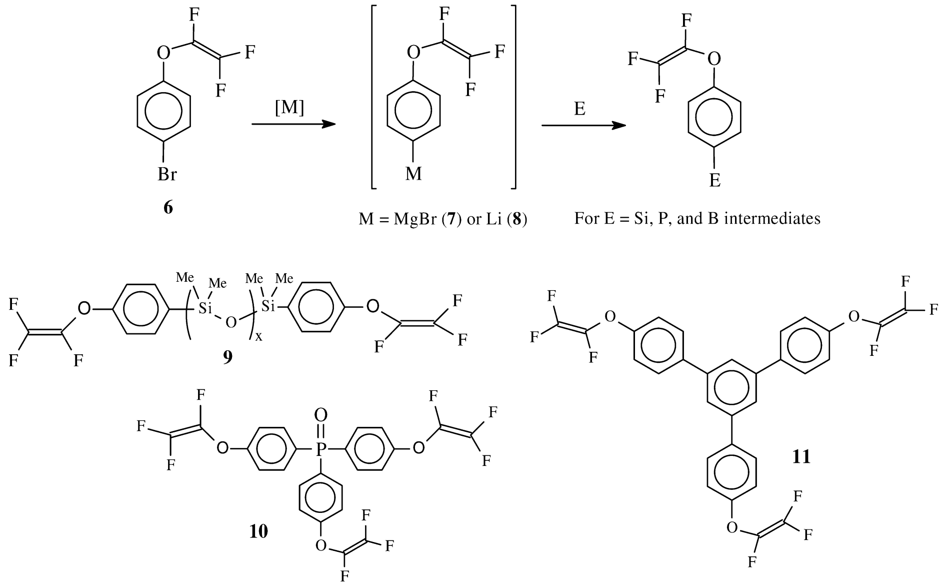


Fig. 2. Trifluorovinyl conversion vs. time for the neat polymerization of **1** at 150°C (reproduced from [5], with permission).



Scheme 3. Monomers prepared by the Intermediate Strategy.

derivatives of phenol, such as 4-bromophenol in order to access a nucleophillic organometalic reagent containing the TFVE group intact (Scheme 3) [4,7,12–14].

This strategy featured the application of the bromo derivative (**6**) which could be easily converted to reactive Grignard (**7**) and lithium (**8**) reagents and thereby access a variety of new inorganic/organic hybrid fluorinated materials amenable to coatings applications. Aryl bromide **6** is easily prepared on the multi-pound per batch scale and is isolated pure by vacuum distillation [4]. Grignard reagent **7** is generated by standard methods and is remarkably stable in THF solution, even at elevated temperatures. The recently discovered aryl lithium reagent **8**, on the other hand, is much more reactive and its formation is more specific [7] (*Caution!* When warmed above −20°C, solutions of TFVE-Li react very exothermically with subsequent decomposition). However, stable solutions are easily prepared and used at low temperature in diethyl ether.

The preparation and use of these nucleophilic organometallic reagents in the presence of electrophilic fluorinated olefins was a surprising result and prompted us to explore theoretical support for their stability. Upon calculating (at the ab initio level) deprotonation energies of trifluorovinyloxy substituted benzene and pyridine model compounds versus the corresponding methyl ether, we found that perfluorovinyl ether stabilizes a *p*-carbanion by as much as 11 kcal/mol and destabilizes the protonated pyridinium analog by 10 kcal/mol [7].

Grignard reagent **7** was first used to prepare a novel disiloxane-containing monomer (**9**, x=1) from which the first elastomeric fluorosilicone PFCB polymers were produced [4]. Subsequently, a range of fluorosilicone PFCB polymers have been prepared. Table 2 exhibits selected properties for polymers prepared from (**9**) for x=1–3.

Alternatively, reaction with trichlorophosphine and subsequent oxidation afforded the first tris-trifluorovinyloxyphenyl phosphine oxide monomer (**10**) which polymerized to a highly thermal and thermal oxidatively stable thermoset [6]. In addition, a completely aromatic example (**11**) was prepared by treatment of **7** with $B(OMe)_3$ and subsequent Pd catalyzed Suzuki coupling with 1,3,5-tribromobenzene [11]. Polyphosphazene networks have also been obtained, from **8**, by either deprotonation/substitution of preformed polyphosphazenes or thermolysis of TFVE functionalized chlorophosphoranimines [14].

Organolithium intermediate **8** was further used to synthesize vinyl derivatives containing the TFVE group [7]. Vinyl derivatives are reacted cleanly with a variety of commercial poly(dimethylsiloxane) co-polymers containing Si–H linkages by employing well known Pt(0) catalyzed hydrosila-

Table 2
Selected properties of PFCB fluorosilicones from monomer **9** in Scheme 3

x	GPC M_n[a]	GPC M_w/M_n[a]	DSC T_g (°C)[b]	TGA T_{onset}(°C)[c]	TGA total loss (%)[c]
1	20 000	3.4	18	434	100
2	12 000	1.6	−19	432	86
3	12 400	1.7	−34	430	86

[a] In THF versus polystyrene.

[b] 10°C/min.

[c] 10°C/min in N_2 to 900°C.

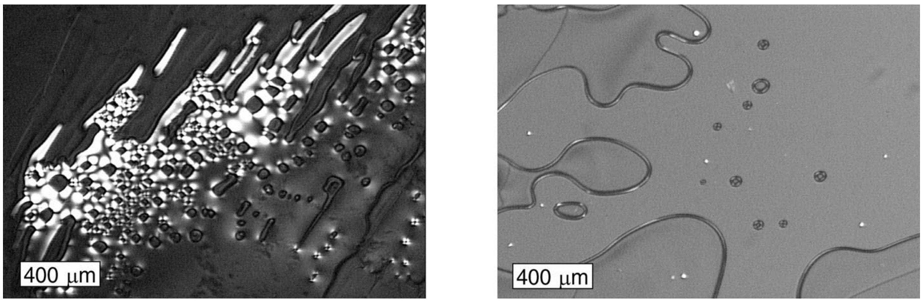


Fig. 3. Optical microscope images of **Poly-4** with (left) and without (right) slight shear.

tion techniques [12–13]. Polymer compositions containing varying amounts of TFVE were obtained based on the amount of Si–H linkages present in the co-polymer. The hydrosilated products ranged from highly viscous liquids to tacky solids depending on the type of pendant attachment and the amount present. Upon heating, pendant TFVE groups cyclodimerize giving new silicone and phosphazene thermosets.

PFCB silicone networks are distinguished from typical commercial fluorosilicones since catalysts and initiators are not required and crosslinking occurs exclusively at the fluorocarbon site. Hybrid thermosets varied in transparency and texture depending on the amount of crosslinking. Free standing films exhibited considerable swelling in organic solvents and FTIR confirmed the distinct presence of the PFCB linkage at 963 cm^{-1} [12–13].

2.3. Liquid crystalline (LC) PFCB coatings

Due to the well-defined nature and unique combination of properties offered by PFCB chemistry, we have further chosen to pursue the synthesis of LC fluoropolymers based on a new TFVE monomer containing the mesogenic α-methylstilbene linkage (**4**, Scheme 2) [23]. In particular, the α-methylstilbene mesogen has been used extensively in a variety of polymeric architectures where most recent attention has been devoted to LC epoxy thermosets [24–26]. Small molecule liquid crystals [27], as well as main and side chain LC polymers [28–29], containing fluorine are also known. The synthesis and LC phase ordering of the new PFCB polymer was studied in an effort to probe the anisotropy of the mesophase and surface orientation as a function of controlled polymer dimensions. For example, semifluorinated PFCB liquid crystals may function well as alignment layers in LC display applications.

Monomer synthesis utilized the traditional phenolic precursor route and polymerization was accomplished by simply heating neat monomer **4** in an inert atmosphere at temperatures above 150°C (Scheme 2). Exothermic cyclodimerization of TFVE groups are typically detected just above 130°C by DSC (10°C/min) as was the case for **4**.

Our initial approach to explore mesophase formation relied on the ability of TFVE polymerization to provide well-defined oligomers with intact reactive terminal groups by a simple heat/quench cycle. LC order was confirmed in **poly-4** by both ^{2}H NMR in the presence of cyclohexane-d_{12}, and polarized optical microscopy. Birefringent textures observed by optical microscopy are consistent with a nematic phase. Slight shear was essential in order to obtain the patterns, which decay with time (Fig. 3). A complete characterization of the homoetropic alignment and relaxation parameters versus surface energy (e.g. Fl incorporation) is currently underway.

2.4. Optical fiber and waveguides

Organic polymer dielectric waveguides are increasingly attractive alternatives to inorganic components in telecommunication devices [30–31]. Polymers offer flexibility, low cost fabrication and connection, high transparency in the visible and near-infrared spectra, and versatility in structure, properties, and grades for task specific integration, such as local-area-network applications. Fluoropolymers, in particular, represent viable alternatives to current optical materials due to their many complementary properties [1,32–33]. Halogenated polymers in general show negligible transmission losses in the range desired and fluoropolymers represent the lowest loss examples of organic polymers to date. DuPont's TeflonTM AF (T_g=160 or 240°C) [3] and Asahi's CYTOPTM (T_g=108°C) [33] are two such amorphous perfluoroplastics for which much interest in low loss optics exist. However, commercial perfluoropolymers in general do not exhibit the thermal and thermomechanical stability required for commercial processes above 250°C. Partially fluorinated polymers, such as polyimides [34], and fluoroacrylate networks [35] have also been reported. Our goal has been to exploit the well-defined polymerization mechanism offered by PFCB chemistry and prepare copolymers with tunable thermal and optical properties [36]. We have found that polymers possessing variable refractive indices, glass transition temperatures (ranging from 165–350°C), and long-term 350°C thermal stability [10] have been accessible by simple choice of comonomer composition (Table 3).

Possible cyclopolymerization rate differences for monomers **1** and **2** (Scheme 2) were first investigated by measuring the olefin consumption during solution polymerization by ^{19}F NMR spectroscopy. Bulk polymerization kinetics for

Table 3
Selected properties of PFCB optical polymers

PFCB polymer from	M_n	M_w/M_n(GPC)	T_g (°C)	n (800 nm)[e]	ε (10 kHz)
1	–	–	350[c]	1.495	2.35
2	50 000[a]	2	165[c]	1.510	2.41
5	60 000	1.9	120	1.3–1.4[f]	–
1-co-2 (50:50) (pregel 24 h rxn)	8000[a]/3200[b]	5	220[d]	1.505	–

[a] NMR end group analysis.
[b] GPC versus PS.
[c] DMS.
[d] Cured to 350°C by DSC.
[e] Abbe refractometer.
[f] Estimated by ellipsometry.

monomer **1** by Raman spectroscopy has also been reported (vide supra) [5]. Fig. 4 shows the ^{19}F NMR spectra for a pre-gelled 50 wt.% co-polymer sample (**1-co-2**) after solution polymerization in mesitylene (50 wt.%) for 24 h at 150°C.

Endgroup analysis by NMR has proven to be a reliable asset in PFCB chemistry [4]. Although the three sets of non-equivalent vinyl fluorine signals (ddd near −120, −127, −134 ppm) overlap surprisingly closely, it was possible to determine from this data and GPC, that the relative rate of disappearance for the two monomers is essentially the same. Fig. 5 graphs the fluoroolefin conversion versus time for the solution (50 wt.% mesitylene) homopolymerization of **1**, **2**, and a 50 wt.% co-polymerization of the two (**1-co-2**) by ^{19}F NMR. From the data in Fig. 5, the rate of cyclopolymerization for **1** and **2** monomer is essentially identical up to one half life at 150°C.

Integration of the multiple non-equivalent cyclobutane fluorines versus the clearly resolved vinyl fluorine, F_a or F_c, gave a n=17 or M_n=8000 for the ideal linear structure shown in Fig. 4. In contrast, M_n=3200 and M_w/M_n=5 was measured by GPC (versus PS) which indicates substantial branching has occurred. After heating to 350°C, a T_g=220°C was measured for the co-polymer by DSC (Table 3).

Polymer samples for optical analysis were prepared by heating neat monomer or a melt mixed monomer mixture (50 wt.%) in glass vials under nitrogen at 200°C for 12–14 h after which near complete conversion of olefin groups had been achieved. The PFCB homopolymers and the co-polymer exhibit low loss in the wavelength range suited for optical waveguide applications (1535–1565 nm). Although quantitative loss measurements have not been determined for **poly-2** and **poly(1-co-2)**, an attenuation of 0.25 dB/cm at 1515–1565 nm has been reported for the **poly-1** [17]. The relative loss data presented here predicts that a similar value may be obtained for the 50 wt.% co-polymer and a slightly higher loss for the **poly-2** and the co-polymers.

The dependence of refractive index on wavelength has been determined for selected homopolymers and co-polymers. As shown in Fig. 6, co-polymerization can be used to tune exact optical properties by monomer composition. In addition, we have recently developed a new TFVE monomer prepared from 4,4′-(hexafluoroisopropylidene)diphenol (**5** in Scheme 2) [37]. The increased degree of fluorination in

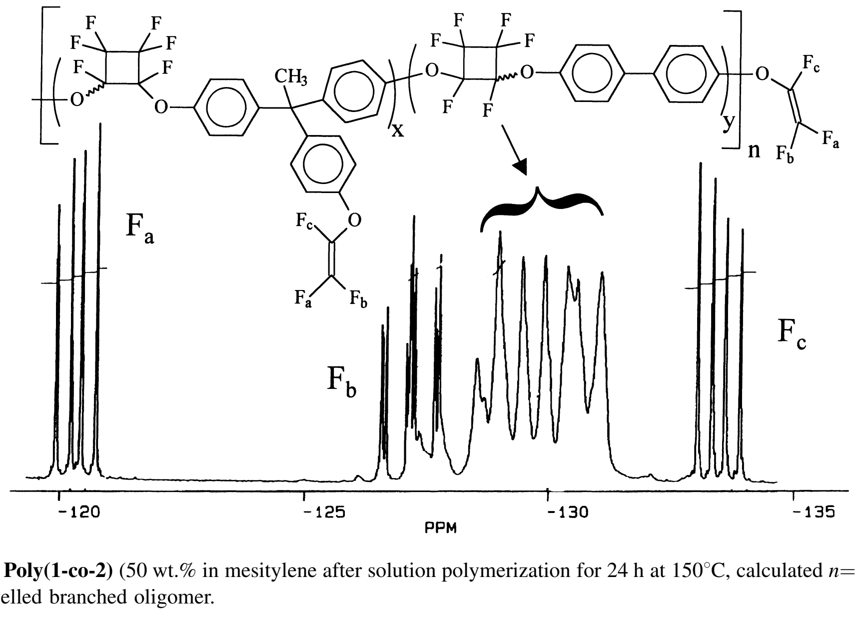


Fig. 4. ^{19}F NMR spectra of **Poly(1-co-2)** (50 wt.% in mesitylene after solution polymerization for 24 h at 150°C, calculated n=17, M_n=8000) and idealized linear structure of the pre-gelled branched oligomer.

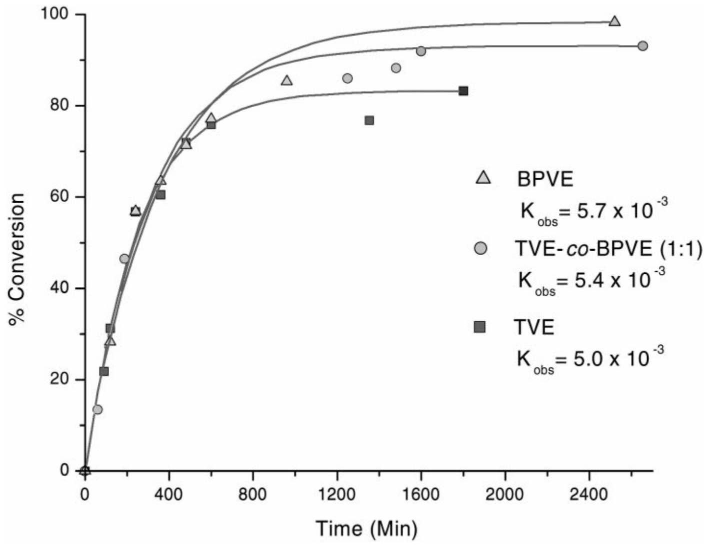


Fig. 5. TFVE conversion vs. time for solution (50 wt.% mesitylene) cyclopolymerization at 150°C by ^{19}F NMR.

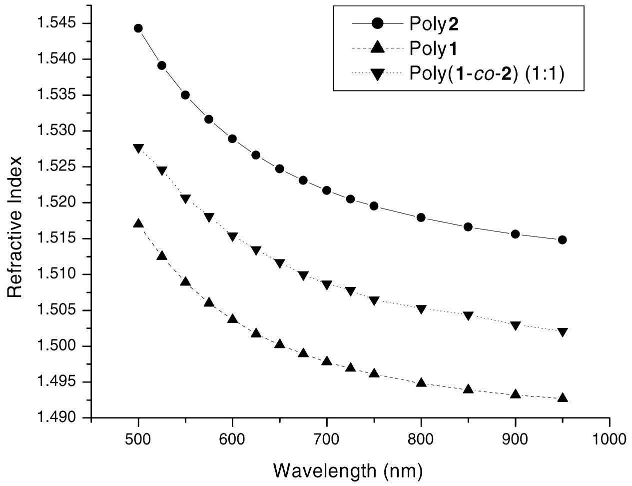


Fig. 6. Refractive index vs. wavelength for selected PFCB polymers.

poly-5 (T_g=120°C) causes a dramatic decrease in the refractive index — well below that previously detected for any PFCB polymer (Table 3). These results indicate that a wide range of materials with tailorable optical and thermal properties can be prepared by judicious choice of comonomer.

3. Experimental

3.1. General information

Bis-phenols were generously provided by the Dow Chemical. Other chemicals and reagents were purchased from Aldrich or Fisher Scientific and used as received unless otherwise stated. ^{1}H NMR 300 MHz and proton-decoupled ^{13}C NMR 75 MHz were obtained on a Bruker AC-300 spectrometer. ^{19}F NMR 188 MHz data were obtained on a Bruker AC-200 spectrometer. Chloroform-d was used as solvent, and chemical shifts reported are internally referenced to tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm), and $CFCl_3$ (0 ppm) for ^{1}H, ^{13}C, and ^{19}F nuclei, respectively. Infrared analyses were performed on neat oils or free standing films using a Nicolet 550 Magna FTIR spectrophotometer. Gas chromatography/mass spectrometry (GC/MS) data were obtained from a Varian Saturn GC/MS. Gel permeation chromatography (GPC) data were collected in THF using a Waters 2690 Alliance System with refractive index detection at 35°C, and equipped with two consecutive Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns. Retention times were calibrated against Polymer Labs Easical PS-2 polystyrene standards. DSC data were obtained from a Mettler–Toledo 820 System under a nitrogen atmosphere at a scan-rate of 10°C/min. Polarized optical microscopy was performed at room temperature using an Omega BX60 optical microscope equipped with a Mettler-Toledo Hot Stage with a magnification of 50x. Raman spectroscopy was performed on polymer samples heated at 150°C in 5 mm NMR tubes [5]. Kinetic data were collected using an ISA U-1000 double monochromator. The 532 nm line of a Coherent Radiation DPSS-200 YAG laser was used as the excitation source. Raman Scattering was collected using a 90° scattering geometry and collected with a charged coupled device. Monomers and polymers were prepared and characterized as generally described for **4** as follows.

3.2. 4,4′-Bis(2-bromotetrafluoroethoxy)-α-methylstilbene

To a 3 l vessel equipped with a Dean–Stark azeotropic distillation assembly were added 1.1 l solution of DMSO, KOH (49.6 g, 0.88 mol), 4,4′-dihydroxy-α-methylstilbene (100 g, 0.44 mol) and 0.35 l of *m*-xylene. Water was removed to less than 500 ppm by azeotropic vacuum distillation at 100°C over 6 h. The vessel was cooled to 20°C and dibromotetrafluoroethane (252.5 g, 0.97 mol) was added dropwise over 3 h and temperature was kept below 10°C throughout the addition. The solution was stirred for 12 h, warmed to room temperature, extracted into 500 ml of hexanes, washed with 3 ml × 100 ml H_2O, and dried over $MgSO_4$. The hexane solution was then flashed over alumina and evaporated giving **1** in 50% yield. ^1H NMR (200 MHz, $CDCl_3$) δ 2.26 (3H, s, *trans* Me), 6.79 (1H, s, *trans* H_v), 7.24 (4 H, m), 7.37 (2H, d, $J=8$ Hz), 7.52 (2H, d, $J=8$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 17.2 (*trans* Me), 108.7 (m, CF_2), 112.9 (m, CF_2), 115.9 (m, CF_2), 116.4, (m, CF_2), 121.4, 126.8, 130.3, 136.6, 137.0, 142.2, 147.3, 148.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ -66.24 (t), -86.60 (t); GC/MS (M^+ Calc. for $C_{19}H_{12}Br_2F_8O_2$ 584.31 g/mol), Obsv. M^+ 584 with distinctive dibromo isotopic mass ratio.

3.3. *4,4′-Bis(trifluorovinyloxy)-α-methylstilbene (**4**)*

To a dry nitrogen purged 1 l vessel was added **1** (129.13 g, 0.22 mol) dropwise to 0.1 l of anhydrous acetonitrile and 30.0 g (0.46 mol) of Zn (30 mesh) at 80°C. The solution was refluxed for 18 h and the acetonitrile was removed from the product/salt mixture in vacuo. The product was removed from the by-product salts by extraction into hexanes and flashed over alumina 3*x* giving **2** as a clear colorless liquid which crystallized upon standing in 58% yield, mp (DSC) 17°C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.17 (trace, s, *cis* Me), 2.23 (3H, s, *trans* Me), 6.78 (1H, s, *trans* H_v), 7.08 (2H, d, $J=3.2$ Hz), 7.09 (2H, d, $J=3.2$ Hz), 7.32 (2H, d, $J=8.7$ Hz), 7.48 (2H, d, 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$), 17.6 (*trans* Me), 26.8, 115.8, 126.4, 127.5, 130.7, 135.0 (ddd, $CF{=}CF_2$, $^1J=110$ Hz, $^2J=156$, 90 Hz), 135.5, 136.2, 147.0 (ddd, $CF{=}CF_2$, $^1J=62$, 276 Hz, $^2J=273$ Hz), 153.7, 154.5; ^{19}F NMR (188 MHz, $CDCl_3$) δ -120 (2F, dd, *cis*-$CF{=}CF_2$, F_a), -127 (2F, dd, *trans*-$CF{=}CF_2$, F_b), -134 (2F, dd, $CF{=}CF_2$, F_c) ($J_{ab}=97$ Hz, $J_{ac}=58$ Hz, $J_{bc}=110$); FTIR (neat): ν 3047, 1898 (w), 1830 (w, $CF{=}CF_2$), 1609, 1514, 1302 (st, br), 1166 (st, br), 843 (w); GC/MS (Calc. for $C_{19}H_{12}F_6O_2$ 386 g/mol), Obsv. *m/z*: 386 (M^+), 191, 165, 152, 115, 89; Anal. Calc. for $C_{19}H_{12}F_6O_2$ (found): C, 59.07 (58.91); H, 3.14 (3.14).

3.4. *PFCB polymer from **4***

To a 50 ml reactor equipped with mechanical stir and nitrogen purge was added 2.0 g of **4**. The neat monomer was degassed via nitrogen sparge and heated at 160°C for 2 h during which time the viscosity increased dramatically and stirring was hindered. Alternatively, polymerization of monomer **2** was accomplished by heating ca. 1.0 g of the solid in an aluminum boat or glass tube. The THF soluble polymer was obtained as a clear solid in essentially quantitative yield. For ^2H NMR and polarized microscopy samples, neat monomer was heated under nitrogen in a 10 mm NMR tube at 155°C with periodic quenching to room temperature. ^1H NMR (200 MHz, $CDCl_3$) δ 2.16 (s, *cis* Me), 2.21 (s, *trans* Me), 6.42 (s), 6.73 (s), 6.86 (br, m), 7.13 (br, d), 7.21 (br, d), 7.29 (br, d), 7.45 (br, d), integration ratio of Me to sum of aromatic and vinylic protons is 3–10; ^{13}C NMR (75 MHz, $CDCl_3$) 17.4, 26.6, 105.9 (m, cyclobutyl-F_6), 109.3 (m, cyclobutyl-F_6), 112.7 (m, cyclobutyl-F_6), 115.4, 117.9, 118.2, 121.4, 125.9, 126.6, 127.2, 127.5, 128.4, 129.6, 134.9, 137.8, 140.6, 140.9, 151.0, 151.7; ^{19}F NMR (188 MHz, $CDCl_3$) δ trifluorovinyl endgroups at -119 (2F, dd, *cis*-$CF{=}CF_2$, F_a), -126 (2F, dd, *trans*-$CF{=}CF_2$ F_b), (2F, dd, $CF{=}CF_2$, F_c) ($J_{ab}=97$ Hz, $J_{ac}=58$ Hz, $J_{bc}=110$); broad cyclobutyl-F_6 at -127.2, -127.6, -128.3, -128.4, -129.0, -129.6, -130.2, -130.5, -130.8 (total cyclobutyl-F); FTIR (neat): ν 3021, 1608, 1515, 1319, 1217, 970 (cyclobutyl-F_6), 775. ^{19}F NMR endgroup analysis for bulk polymerization (150°C for 3 h, 200°C for 12 h) gave 91% olefin conversion and avg. DP $(n)=10$, or $M_n=4200$. GPC analysis found $M_w>110{,}000$ and $M_w/M_n>20$. Reproducible glass transition temperatures are not observed for soluble oligomers, yet heating to 300°C resulted in an insoluble film with a DSC (10°C/min) measured $T_g=110$°C.

Acknowledgements

We thank Clemson University, The Dow Chemical Company, 3M Corporation for supporting this work, and Mettler-Toledo for donation of a DSC820 system to Clemson University. Prof. R. Neilson, Dr. S. Narayan-Sarathy, and Dr. J. Ji at Texas Christian University, and Dr. J. Laanne and S.-N. Lee at Texas A & M University for collaboration in part. We also acknowledge R.V. Snelgrove, Dr. K. Clement, Dr. C.M. Cheatham D., and Dr. B. Ezzell at the Dow Chemical Company for their pioneering efforts in PFCB chemistry.

References

[1] A.E. Feiring, in: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994, p. 339.

[2] M. Yamabe, in: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994, p. 397.

[3] P.R. Resnick, W.H. Buck, in: J. Scheirs (Ed.), Modern Fluoropolymers, Wiley, New York, 1997, p. 397.

[4] D.W. Smith Jr., D.A. Babb, Macromolecules 29 (1996) 852.

[5] C.M. Cheatham, S-N. Lee, J. Laane, D. Babb, D.W. Smith Jr., Polym. Int. 46 (1998) 320.

[6] D.A. Babb, H. Boone, D.W. Smith Jr., Rudolf J. Appl. Polym. Sci. 69 (1998) 2005.

[7] J. Ji, S. Narayan, R. Neilson, J. Oxley, D. Babb, N. Rondan, D.W. Smith Jr., Organometallics 17 (1998) 783.

[8] D.A. Babb, B.R. Ezzell, K.S. Clement, W.F. Richey, A.P.J. Kennedy, Polym. Sci.: Part A: Polym. Chem. 31 (1993) 3465.

[9] A.P. Kennedy, D.A. Babb, J.N. Bremmer, A.J.J. Pasztor Jr., Polym. Sci.: Part A: Polym. Chem. 33 (1995) 1859.

[10] D. Babb, V. Snelgrove, D.W. Smith, Jr., S. Mudrich, in: J. Hedrick, J. Labadie (Eds.), Step-Growth Polymers for High Performance Materials, ACS Sym. Ser., No. 624, American Chemical Society, Washington, DC, 1996.
[11] H.W. Boone, D.W. Smith Jr., D.A. Babb, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. 39 (2) (1998) 812.
[12] S. Narayan, J. Ji, R.H. Neilson, D.W. Smith Jr., Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 39 (1) (1998) 530.
[13] S. Narayan, R.H. Neilson, D.W. Smith Jr., Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 39 (1) (1998) 609.
[14] R.H. Neilson, J. Ji, S. Narayan-Sarathy, D.W. Smith Jr., D.A. Babb, Phosphorous, Sulfur and Silicon 144 (1999) 221.
[15] D.J. Perettie, L.D. Bratton, J.N. Bremmer, D.A. Babb, in: Proceedings of International Symposium on Electronic Imaging: Science and Technology, IS&T/SPIE, 1993, pp.1911–03.
[16] C.W. Kim, C.O. Jeong, S.K. Rho, J.H. Lee, H.R. Nam, J.H. Choi, M.P. Hong, S.Y. Kim, H.G. Yang, J.H. Souk, in: Proceedings of Symposium on Society for Information Display (SID), Display Manufacturing Technology Conference, January 1997.
[17] G. Fishbeck, R. Moosburger, C. Kostrzewa, A. Achen, K. Petermann, Electron. Lett. 33 (6) (1997) 518.
[18] D.J. Perettie, D.A. Babb, Q. Chen, J.H. Judy, in: Proceedings of Symposium on IEEE Magnetics, MMM-Intermag Conference, 1994, DQ-08.
[19] T.A. Tumolillo Jr., A. Thomas, P.R. Ashley, Appl. Phys. Lett. 82 (24) (1993) 3068.
[20] P. Townsend, E. Shaffer, M. Mills, J. Blackson, M. Radler, in: A. Lagendijk, H. Treichel, K. Uram, A. Jones (Eds.), Low-Dielectric Constant Materials II, Mat. Res. Soc. 443 (1996) 35.
[21] B.E. Smart, in: R.E. Banks, B.E. Smart, J.C. Tatlow, (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994, p. 73.
[22] B. Atkinson, A.B. Trentwith, J. Chem. Soc. (1953) 2082.
[23] D.W. Smith Jr., H.W. Boone, R. Traiphol, H. Shah, D. Perahia, Macromolecules 33 (4) (2000) 1126.
[24] C. Ortiz, R. Kim, E. Rodighiero, C.K. Ober, E.J. Kramer, Macromolecules 31 (1998) 4074.
[25] B.C. Beniceicz, M.E. Smith, J.D. Earls, R.D. Priester, S.M. Setz, R.S. Duran, E.P. Douglas, Macromolecules 31 (1998) 4730.
[26] J. Liu, C. Wang, G. Campbell, J. Earls, R. Priester, J. Polym. Sci.: Polym. Chem. 36 (1998) 1457.
[27] T. Inoi, in: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994, p. 263.
[28] J.C. Wittmann, S. Meyer, P. Damman, M. Dosiere, H-W. Schmidt, Polymer 39 (15) (1998) 3545.
[29] M. Sato, S. Ujiie, Y. Tada, Y. Goto, J. Polym. Sci. Part A: Polym. Chem. 36 (1998) 1243.
[30] B.L. Booth, J. Lightwave Technol. 7 (10) (1989) 1445.
[31] A.C. Levy, C. Taylero, in: J. Kroschwitz (Ed.), Encycl. Polym. Sci. and Eng, Vol. 7, Wiley, New York, 1987, pp. 1–15.
[32] T. Kaino, J. Polym. Sci. Part A 25 (1987) 37.
[33] N. Sugiyama, in: J. Scheirs (Ed.), Modern Fluoropolymers, Wiley, New York, 1997, p. 541.
[34] T. Matsuura, S. Ando, S. Sasaki, F. Yamamoto, Electron. Lett. 29 (3) (1993) 269.
[35] A. Hale, K. Quoi, D. DiGiovanni, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 39 (2) (1998) 978.
[36] H. Shah, A. Hoeglund, M. Radler, C. Langhoff, D.W. Smith Jr., Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 40 (2) (1999) 1293.
[37] D.W. Smith, Jr., H. Shah, B. Johnson, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 41(1) (1998), in press.