Synthesis and Characterization of Poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]]

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ABSTRACT: A new high-performance material, poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]] (PDTFE), was prepared by Ni(0)-catalyzed coupling of 2,2-bis(*p*-chlorophenyl)-hexafluoropropane. The resulting high molecular weight polymer ($\bar{M}_n$ of 19.2×10^3 g/mol by gel permeation chromatography and 27.5×10^3 g/mol by multiple-angle laser light scattering) is amorphous and soluble in a number of common organic solvents including tetrahydrofuran, chloroform, and acetone. The solubility leads to ease of preparation, characterization, and processing of PDTFE. Excellent thermal properties were exhibited with a glass transition temperature of 255 °C and 10% weight loss values of 533 and 535 °C in nitrogen and air, respectively. The flame-retardant properties showed that the material meets the Federal Aviation Administration's current criteria for heat release capacity, total heat release, and char yield for flame-retardant materials. Additionally, colorless, transparent, creasable films were cast from chloroform. The film formation of PDTFE made the gas permeability measurements possible. PDTFE has a rather high oxygen permeability coefficient of 120×10^{-10} cm^3 (STP)cm/(cm^2·s·cmHg) and an O_2/N_2 selectivity of 2.9 at 35 °C. The new material has an impressively low dielectric constant of 2.56. Finally, the new polymer is highly hydrophobic with no detectable water uptake after 24 h in boiling water. The combination of facile synthesis and an excellent property profile makes this a unique phenylene-based high-performance polymer that will lead to a series of novel fluorinated materials.

Introduction

The coupling of aryl halides using the Ni(0)-catalyst system was first reported by Colon and Kelsey to quantitatively convert chlorobenzene to biphenyl.[1] Since their work, several researchers have extended this reaction to polymerizations, which produced high-performance materials. Percec et al.[2−5] demonstrated that Ni(0)-catalyzed coupling successfully synthesizes functional poly(*p*-phenylene)s. Conducting and nonlinear optically active polymers have been synthesized utilizing nickel-catalyzed coupling polymerization as demonstrated by Ueda et al.[6]

Formation of aromatic carbon−carbon bonds via the Ni(0)-catalyzed coupling reaction can also be used to synthesize high-performance polymers with functional groups in the backbone. Colon et al.[7] demonstrated that high molecular weight poly(arylene ether sulfone)s could be made by this method. Ueda et al.[8,9] also utilized the mild reaction conditions of the Ni(0) route to produce poly(arylene ether sulfone)s, as well as several poly(arylene ether ketone)s. More recently, McGrath and Ghassemi demonstrated that the Ni(0) reaction could be used to incorporate phosphine oxide groups into a polymer backbone, yielding novel poly(arylene phosphine oxide)s.[10]

Our interest in high-performance polymers via nickel-catalyzed coupling has led us to various poly(*p*-phenylene) (PPP) derivatives, including poly(2,5-benzophenone)s, poly(2,5-diphenyl sulfone)s, and poly(2,5-thiophene)s.[11−16] In each case, nickel catalysis polymerization was utilized due to the ease of aromatic carbon−carbon bond formation and the ability to incorporate a variety of useful functional groups. Recently, using the nickel route, our synthetic targets have become new fluorinated materials.

Introduction of fluorine into previously reported high-performance polymers significantly improved polymer properties.[17] In some cases, fluorine contributed to increased thermal properties of polyimides and polyethers, yielding materials with glass transition temperatures greater than 400 °C.[18] The solubility of poly(*p*-phenylene) was improved by the addition of small fluorinated substituents as pendant groups. The resulting polymers have 10% weight loss values of approximately 550 °C in nitrogen.[19] When fluorine was incorporated into polyimides, flame-retardant polymers with increased hydrophobicity were the result.[20] These polymers showed large contact angles and decreased water absorption. The same polyimides exhibited lower dielectric constants in the range 3.2−2.6 as the amount of fluorine was increased.

The incorporation of hexafluoroisopropylidene [$C(CF_3)_2$] linkages into the backbone of a wide variety of glassy, aromatic polymers (polysulfones,[21] polycarbonates,[22] polyimides,[23] and polyamides[24]) resulted in polymers with higher gas permeability coefficients at similar selectivity values than the analogous polymers with only isopropylidene [$C(CH_3)_2$] linkages. The objective of material design for gas separation polymers is to produce polymers that are more permeable and more selective than existing materials.[25,26] In this regard, the hexafluoroisopropylidene group has emerged as an important chemical unit for enhancing gas separation properties of amorphous, aromatic polymers.

The goal of the present investigation is to exploit the mild temperature nickel-catalysis solution polymerization technique to introduce property-enhancing fluorine

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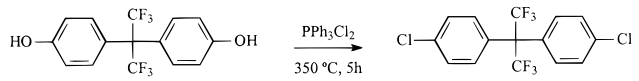
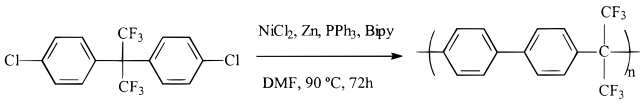
Scheme 1. Synthesis of 2,2-Bis(*p*-chlorophenyl)hexafluoropropane



I

Scheme 2. Synthesis of Poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]]



II

atoms into materials with high thermal stability. The target polymer contains only benzene rings and the hexafluoroisopropylidene linkage. The unique structure permits characterization of the polymer properties without the influence of other functional groups (ketones, ethers, imides, sulfones, etc.). The 6F-based polymer described herein is the first in this new series of fluorinated high-performance polymers with excellent thermal properties, film-forming ability, low dielectric constant, low moisture absorption, and excellent flame retardance. The optimized synthesis of the polymer is described. In addition, each of these property assumptions is tested and verified. Finally, the gas permeability of the polymer is reported for a number of typical gases. These properties are compared to those of other fluorinated and nonfluorinated membrane-forming polymers.

Experimental Section

Materials. All reagents were purchased from Aldrich and used as received unless otherwise indicated. Dipyridyl and triphenylphosphine were purified by recrystallization from ethanol. All compounds synthesized were purified until their ^{1}H NMR spectra corresponded to the expected structure and purity was greater than 99% by DSC melting point and GC/MS.

2,2-Bis(*p*-chlorophenyl)hexafluoropropane (Scheme 1). To a 250 mL round-bottom flask equipped with a nitrogen inlet was added dichlorotriphenylphosphorane (35.7 g, 107 mmol) and 4,4′-(hexafluoroisopropylidene)diphenol (18.1 g, 53.6 mmol). The flask was placed in a heating mantel, insulated with sand, and heated to 350 °C for 4 h. The reaction temperature was monitored with a thermocouple. The brown reaction mixture was cooled to room temperature and dissolved in methylene chloride. The resulting solution was eluted through a short basic aluminum oxide column using hexane as the eluting solvent. The product was distilled, and 12.4 g (33.2 mmol, 62%) of white solid formed: mp = 60 °C (DSC). ^{1}H NMR: δ 7.35 (d, J = 8.7 Hz, 4H), 7.29 (d, J = 8.7 Hz, 4H). ^{13}C NMR: δ 135.89 (C-4), 132.72 (C-1), 131.73 (C-3), 128.87 (C-2), 124.12 (quartet, J = 1140 Hz, C-6), 64.55 (septet, J = 102.3 Hz, C-5). ^{19}F NMR: δ −60.58 (singlet). ^{31}P NMR showed only the reference peak. The theoretical weight percents are 48.29% C and 2.14% H. Elemental analysis showed 48.25% C and 2.16% H. Theoretical mass was calculated to be 371.990 73 g/mol; high-resolution mass spectrometry showed a measured mass of 371.990 44 g/mol with a deviation of −0.78 ppm.

Poly[[1,1′-biphenyl]-4,4′diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]] (Scheme 2). PDTFE was synthesized in the following manner. To a three-necked 250 mL pear-shaped flask equipped with an overhead stirrer was added zinc (2.17 g, 3.32 × 10^{-2} mol), nickel chloride (0.104 g, 8.03 × 10^{-4} mol), triphenylphosphine (2.8 g, 1.07 × 10^{-2} mol), and dipyridyl (0.1253 g, 8.03 × 10^{-4} mol). *N*,*N*-Dimethylformamide (DMF) (10 mL) was added via syringe, and the mixture was stirred at 80 °C until a deep red-brown color was observed. At that time, 2,2-bis(*p*-chlorophenyl)hexafluoropropane (4.00 g, 1.07 × 10^{-2} mol) was added. The reaction continued at 90 °C for 72 h. The catalyst was quenched by pouring the reaction mixture into 400 mL of 25% HCl/methanol solution and stirred overnight. The polymer was filtered and rinsed with a 10% sodium bicarbonate solution, dissolved in 30 mL of chloroform, and reprecipitated in 400 mL of methanol. The polymerization gave 95% yield of a white powder. ^{1}H NMR: δ 7.62 (d, J = 8.1 Hz, 4H), 7.50 (d, J = 8.1 Hz, 4H). ^{13}C NMR: δ 140.51 (C-4), 133.00 (C-1), 130.84 (C-3), 126.94 (C-2), 124.28 (quartet, J = 1134 Hz, C-6), 64.41 (septet, J = 100.8 Hz, C-5). ^{19}F NMR: δ −60.27 (singlet). ^{31}P NMR showed only the reference peak. The theoretical weight percents are 59.61% C and 2.67% H. Elemental analysis showed 59.38% C and 2.59% H.

Characterization. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR (hexafluorobenzene as the reference) were measured in $CDCl_3$ with a Bruker 400 MHz spectrometer. ^{31}P NMR (phosphoric acid as the reference) was measured in acetone. A Varian gas chromatograph fitted with a Finnigan Mat Magnum mass spectrometer was used for product identification and purity confirmation. High-resolution mass spectrometry was performed with a Kratos MS50TC at a resolution (R) of 14 300 in electron impact (EI) mode with an electron beam energy of 70 eV. Monomer melting points and polymer glass transition temperatures were determined using a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) at a heating rate of 20 °C/min and a heating range of 25−350 °C, with nitrogen purge. Glass transition temperatures were reported as the inflection point of the change in heat capacity during the second heat. Thermogravimetric analyses (TGA) were performed on Perkin-Elmer TGA with heating rates of 10 °C/min. Molecular weights were determined by gel permeation chromatography (GPC) and multiple-angle laser light scattering (MALLS) using a Waters gel permeation system coupled with a Wyatt miniDAWN. The chromatography system was equipped with three Waters styragel columns, and measurements were made at 40 °C with THF as the solvent at a flow rate of 1.0 mL/min. Molecular weights (GPC) were calculated with a calibration plot constructed with polystyrene standards. The UV−vis absorption spectrum was obtained with a Shimadzu UV-2101PC UV−vis scanning spectrophotometer. Elemental analysis of the monomer and polymer was performed using a Perkin-Elmer model 2400 series II CHN/S instrument. Wide-angle X-ray diffraction (WAXD) experiments were conducted using a Phillips diffractometer. Diffraction data were collected in the range 10° < 2θ < 75° with a step size of 0.05° (2θ) and a counting time of 10 s per step using Cu Kα radiation. The contact angle was measured using a Ramé-Hart goniometer equipped with an image analysis attachment.

Thin polymer films were prepared by dissolving 0.15 g of polymer in 4 mL of chloroform followed by pouring into a 5 × 60 mm evaporating dish. The films were allowed to form overnight and dried to remove residual solvent. Film density was determined on the basis of film weight and volume at ambient conditions. The density data were used to characterize chain packing by estimating the fractional free volume (FFV), which was calculated using the following relation:

$$\mathrm{FFV} = \frac{V - 1.3V_w}{V}$$

where V is the polymer specific volume, and V_w is the specific van der Waals volume calculated using the group contribution method suggested by Van Krevelen.[27] Pure gas permeabilities of these polymer films were determined at 35 °C using the constant pressure/variable volume method.[28] The gases used were hydrogen, helium, nitrogen, oxygen, methane, and carbon dioxide. The feed pressure was 50 psig except for methane (methane: 100 psig), and the permeate pressure was maintained at 0 psig [i.e., $p_2 - p_1$ = 50 psig = 3.4 atm, $p_2 - p_1$ = 100 psig = 6.8 atm (methane)]. The permeability coefficients are reported in barrers, where 1 barrer = 10^{-10} cm^3 (STP) cm/(cm^2·s·cmHg).

Results and Discussion

2,2-Bis(*p*-chlorophenyl)hexafluoropropane (I). The monomer was selected because of the enhanced

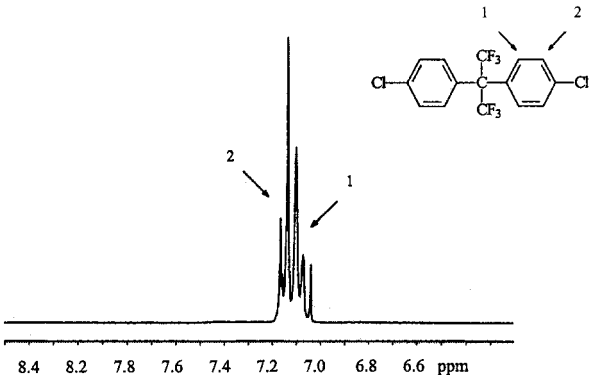


Figure 1. Proton NMR of 2,2-bis(*p*-chlorophenyl)hexafluoropropane.

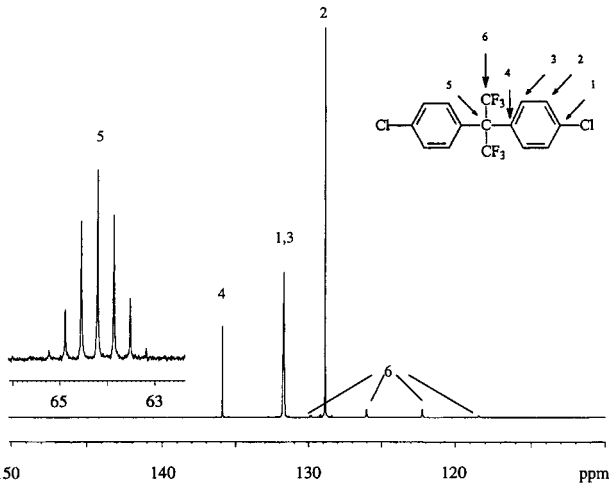


Figure 2. Carbon NMR of 2,2-bis(*p*-chlorophenyl)hexafluoropropane.

properties expected upon incorporation of fluorine. It was prepared according to a previous patent that described the nucleophilic substitution reaction of dibromotriphenylphosphorane and 4,4′-(hexafluoroisopropylidene)-diphenol.[29] **I** was soluble in hexane, chloroform, acetone, tetrahydrofuran, methylene chloride, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, dimethyl sulfoxide, and methanol and partially soluble in ethanol. Due to the monomer's high solubility, recrystallization was difficult. Therefore, it was further purified by distillation to ensure polymer grade monomer. The monomer exhibited a sharp melting point at 60 °C, determined by DSC. The GC-MS showed only one peak in the gas chromatogram. In the mass spectrum, the parent peak along with characteristic fragment peaks was present. High-resolution mass spectra and elemental analysis data further confirmed the chemical composition of **I**.

NMR verified the chemical structure of **I**. Proton NMR **(**Figure 1) showed two doublets. The doublet at δ 7.35 was further split by ortho-benzene coupling, while the doublet at δ 7.29 was broadened by the CF_3 groups. ^{13}C NMR (Figure 2) showed a quartet for C-6, and the quaternary aliphatic carbon, C-5, was split into a septet due to the two CF_3 groups. Carbons marked as 1 and 3 gave very similar chemical shifts in the monomer and appeared to be one peak in the carbon NMR spectrum. Correct assignments for each proton were made with the aid of 2D NMR.

Poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]] (II). For the polymerization of **I,** we referred to Colon's original paper in which he first utilized the Ni(0)-catalyst to couple aromatic chlorides.[1] Reaction conditions for the polymerization of **I** were optimized by varying the solvent, solvent volume, reaction time, temperature, and catalyst ratio. It was found that excessively pure and dry reagents were needed to produce high molecular weight. Only when *N*,*N*-dimethylformamide was used as the polymerization solvent could high molecular weight be achieved. In addition, it was found that when a molar equivalent of triphenylphosphine to monomer was added, the best results were obtained. Excess zinc in the ratio of 3.1:1 to monomer also improved the molecular weight. High molecular weights were only obtained with a reaction time of 72 h. To verify that the CF_3 groups were still present and no side reactions occurred, ^{19}F NMR and ^{31}P NMR were taken of the monomer and the polymer and then compared. For both samples only the reference peak of the phosphoric acid was observed in ^{31}P NMR. ^{19}F NMR showed a singlet at δ −60.58 for the monomer and a singlet at δ −60.27 for the polymer.

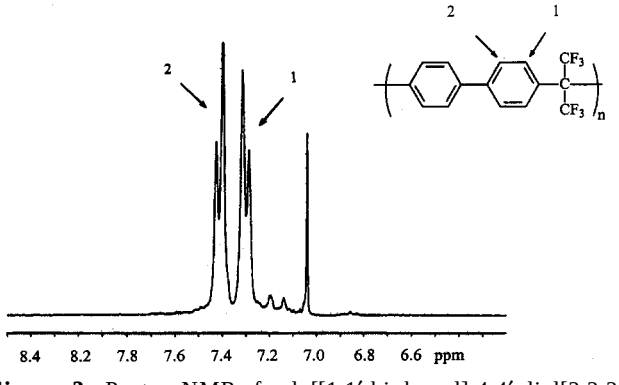


Figure 3. Proton NMR of poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]].

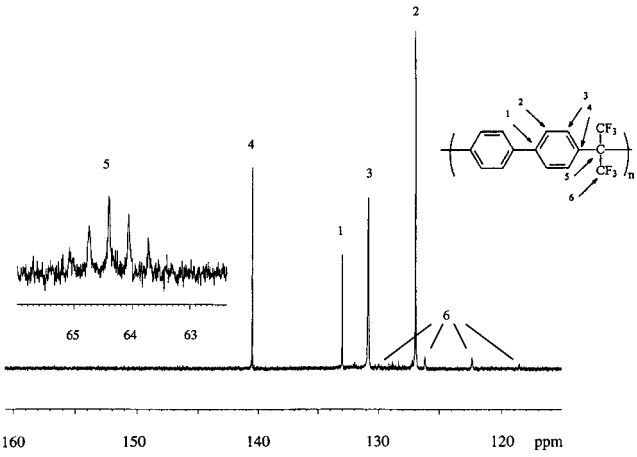


Figure 4. Carbon NMR of poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]].

The chemical structure of **II** was verified by NMR and UV−vis spectroscopies. Proton NMR (Figure 3) showed two doublets and two broad smaller peaks. The doublet peaks were broader than the peaks present in the spectra of the monomer and no longer show any effects of ortho coupling. Each of the two smaller peaks present between δ 7.1 and δ 7.2 were attributed to polymer end groups and were used to calculate the degree of polymerization. ^{13}C NMR (Figure 4) showed a quartet for the CF_3 groups and a septet for the quaternary aliphatic carbon due to the CF_3 groups. Carbons marked as 1 and 3 were separated because of the change in chemical

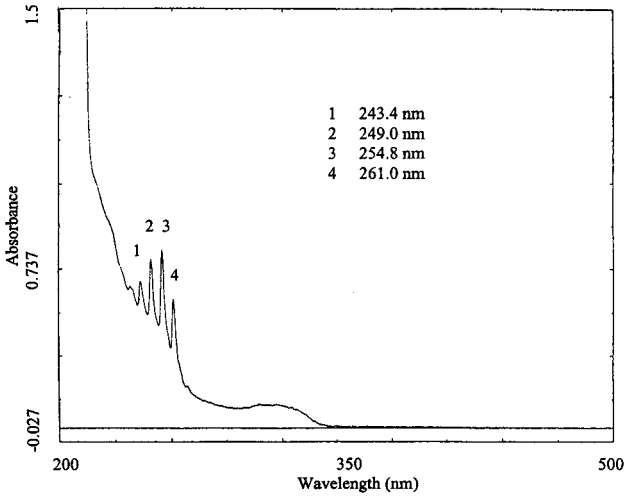


Figure 5. UV−vis trace of poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]].

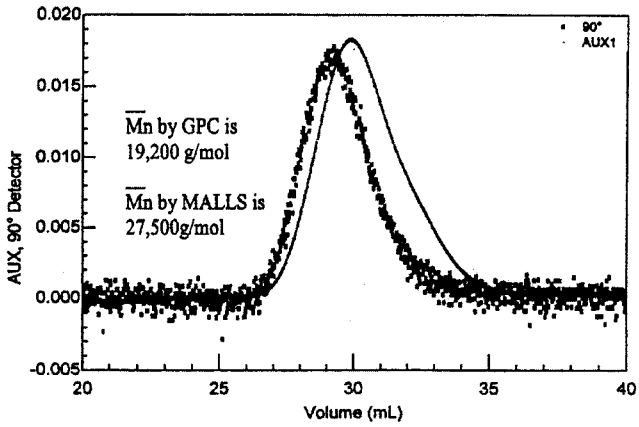


Figure 6. (—) GPC and (- - -) MALLS chromatograms of poly-[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]].

shifts once the polymer was formed; carbon 1 is now further downfield. The small peaks present between δ 127−129 were also attributed to end groups. Once again, 2D NMR was used to verify the correct assignments in the proton NMR. The polymer is white with a λ_{max} value of 254.8 nm in chloroform solution, and no absorption occurs above 340 nm (Figure 5). Reported polyimides containing the BisAF units were pale yellow,[30] signifying longer conjugation lengths than **II**.

Surprisingly, **II** is completely soluble at room temperature in a number of common organic solvents such as chloroform, acetone, tetrahydrofuran, methylene chloride, and *N*,*N*-dimethylformamide; **II** is insoluble in hexane, methanol, and ethanol.

II has a number-average molecular weight of 19.2 × 10^3 g/mol by GPC and 27.5 × 10^3 g/mol by MALLS (d*n*/d*c* = 0.075 mL/g in THF at 40 °C). The degree of polymerization (DP) determined by light scattering is 91. This is in good agreement with the DP calculated from end group analysis by proton NMR, which is 95. The GPC and MALLS chromatograms are shown in Figure 6. Poly(2,5-benzophenone)s previously prepared had lower molecular weight values by MALLS than by GPC.[12] The hydrodynamic volume for such rigid-rod polymers probably influences the molecular weight correlations, resulting in a large deviation between the two methods. Since the GPC data reflect the hydrodynamic volume based on polystyrene standards, the

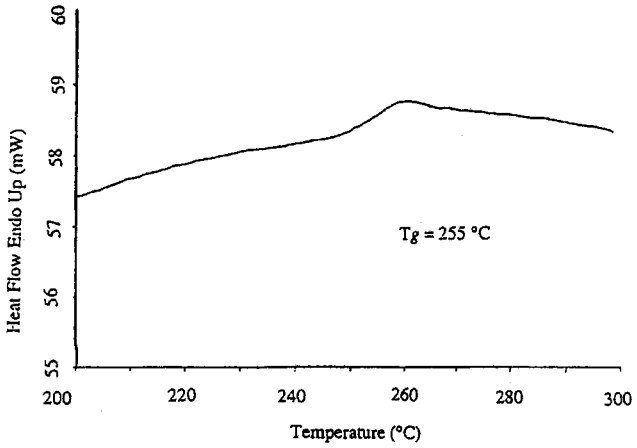


Figure 7. DSC thermogram of poly[[1,1′-biphenyl]-4,4′-diyl-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]].

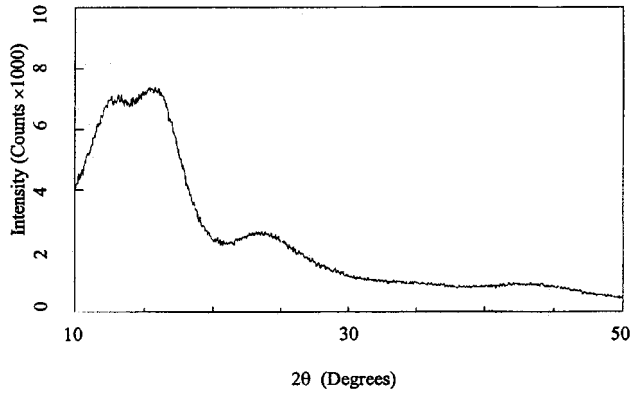


Figure 8. WAXD pattern of poly[[1,1′-biphenyl]-4,4′-diyl-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]].

MALLS data more accurately reflect the molecular weight of **II**. PDTFE has a polydispersity index of 1.61 by GPC and 1.25 by MALLS. The deviation from the theoretical value of 2.0 is consistent with other polymers prepared by Ni(0) catalysis and may be due to the loss of some lower molecular weight polymer during work-up.[3,4,12,18]

The 6F polymer has a glass transition temperature (T_g) of 255 °C, shown in Figure 7. Poly(arylene ether sulfone) with the same BisAF component has a substantially lower T_g, 180 °C, presumably due to the flexible ether linkages. PDTFE exhibits no evidence of crystallinity by DSC or by wide-angle X-ray diffraction (Figure 8). The WAXD pattern shows an amorphous halo. There are two peaks at 2θ between 10° and 20°.

Thermogravimetric analysis (Figure 9) showed 5% weight loss values at 515 °C for both nitrogen and air. It also showed 10% weight loss values at 533 °C in nitrogen and 535 °C in air. The thermal stability of PDTFE is comparable to the polyimide based on 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl and 1,4-bis-(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydrides.[32] This particular polyimide has a T_g of 332 °C and 5% weight loss at 569 °C in nitrogen and 549 °C in air. Our new polymer has only slightly lower 10% weight loss numbers. However, the new 6F polymer has better solubility than these polyimides, which should improve processing.

Isothermal gravimetric analysis was performed on the high molecular weight polymer, and the data collected are shown in Table 1. It is important to note that at

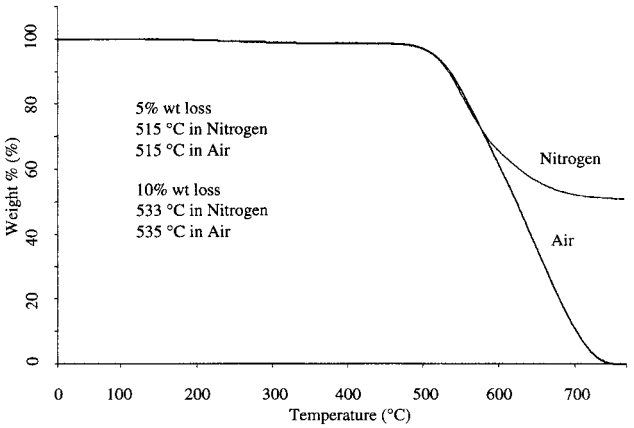


Figure 9. TGA thermograms of poly[[1,1′-biphenyl]-4,4′-diyl-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]].

Table 1. Isothermal Gravimetric Analysis of Poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]][a]

temp (°C)	initial wt (mg)	final wt (mg)	% wt loss/h
300	12.059	12.059	0
350	4.966	4.948	3.6×10^{-5}
400	7.722	7.484	0.031

[a] Data collected for 100 h in nitrogen at indicated temperature.

Table 2. Polymer Flammability[a]

polymer	heat release capacity (J/(g K))	total heat released (kJ/g)	char yield (%)
Nylon 6-6	348	32	0
PMMA	297	25	0
KEVLAR	170	14	35
RADEL R	92	12	52
TORLON	28	6	64
new 6F polymer	25	3	50
KAPTON	14	4	66
PBO	3	1	97

[a] Data taken from the FAA Data Base on Fire Resistant Materials.

300 and 350 °C virtually no weight loss occurs. After 100 h at 400 °C only 0.03% of the initial weight is lost.

PDTFE has a heat release capacity of 25 J/(g K), a total heat of combustion of volatiles of 3.3 kJ/g of solid, and a pyrolysis residue of 50.4% at 650 °C. These values are preliminary numbers obtained on a prototype device. The residual mass fraction was determined by a rapid heating rate of 200 °C/min to 650 °C followed by an isothermal hold for 5 min.[33−35] Table 2 lists a Federal Aviation Administration ranking of fire-resistant polymers. These values were obtained on a prototype device and are currently being validated. Our new polymer is comparable to other high-performance polymers with respect to microscale heat release capacity. The fire-resistant values for the new 6F material surpass the values for RADEL R (polyphenylsulfone) and are more comparable to TORLON (polyamideimide). Although TORLON exceeds the char yields of PDTFE, PDTFE does surpass the FAA char yield requirement of 45%. The FAA's future goal is to find a material with a heat release capacity of 8 J/(g K), a total heat of combustion of volatiles of 1 kJ/g of solid, and a pyrolysis residue of 45% at 650 °C. Our new polymer has only slightly higher values for the heat release capacity and total heat of combustion for the FAA's future goals. On the basis of existing correlations, it would be expected to meet or exceed the FAA's current requirement for flaming heat release rate when tested according to FAR 25.853(a-1) Heat Release Rate Test for Aircraft Cabin Materials.

Table 3. Gas Permeability of Poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]

gas	permeability coeff (barrers)[a]	gas	permeability coeff (barrers)[a]
He	390	O_2	120
H_2	470	N_2	41
CO_2	470	CH_4	34

[a] 1 barrer = 1×10^{-10} cm^3 (STP)cm/(cm^2 s cm Hg). Film thickness: 30.3 μm.

Water absorption data and contact angles were measured. After 100 h submerged in distilled water, films showed virtually no increase in weight at temperatures of 25, 35, 45, and 55 °C. At 8, 12, and 24 h in boiling water, the films showed no detectable changes in appearance or weight. With the highly nonpolar aromatic rings and the hydrophobic fluorine atoms, the films do not absorb significant amounts of moisture. Immediately after a drop of water was placed on a PDTFE film, the contact angle measured was 73.9°. The dielectric constant for the 6F polymer was 2.56. Several fluorinated polyimides showed higher dielectric constants ranging from 2.6 to 3.2.[20] However, moisture absorption was cited as a problem. Once the polyimides absorbed moisture, the dielectric constants increased to 2.8−3.6. The highly hydrophobic nature of the new 6F polymer ensures that the dielectric constant will not be significantly influenced by humidity.

Films of this polymer prepared from a chloroform solution were colorless, transparent, and flexible. The fractional free volume (FFV) was estimated to be 0.29 using an average film density of 1.24 g/cm^3. On the basis of repeated measurements of density, the uncertainty in the average FFV is ±0.01. This FFV value is much higher than that of low-permeability, conventional, glassy polymers such as polysulfone (0.16) and polycarbonate (0.17).[36] The FFV is the same as that of highly permeable glassy polymers such as poly(1-trimethylsilyl-1-propyne) [PTMSP] (0.29) and is similar to the FFV values of random copolymers of tetrafluoroethylene [TFE] and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole [PDD] (0.32 for PPD 87 mol % and 0.28 PPD 65 mol %).[37]

Table 3 summarizes permeability coefficients of this polymer film to various gases at 35 °C. Consistent with the high fractional free volume value, the permeability coefficient to oxygen was 120 barrers, which is very high relative to conventional glassy, aromatic polymers. In fact, this polymer is the most permeable glassy, hexafluoroisopropylidene-containing polymer known. The O_2 permeability of PDTFE is similar to that of other very high free volume, glassy, fluorinated polymers. For example, poly(TFE-*co*-PDD) (PDD content = 65 mol %, DuPont AF1600) has an O_2 permeability of 365 barrers. These values are lower than those of the most permeable fluoropolymer known, poly(TFE-*co*-PDD) (PDD content = 87 mol %: DuPont AF2400), which has an O_2 permeability coefficient of 1380 barrers. Moreover, the permeability is substantially lower than that of the most permeable polymer known, PTMSP, which has an O_2 permeability of 9860 barrers.[37,38] While all of these polymers are stiff chain, glassy polymers and have very high free volume, subtle differences in the distribution

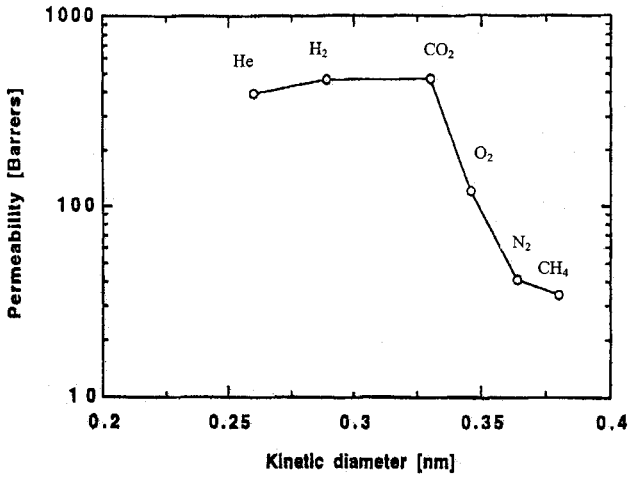


Figure 10. Permeability coefficients as a function of penetrant kinetic diameter at 35 °C.

of free volume elements probably also play a large role in determining gas permeation properties.

Figure 10 presents gas permeability coefficients as a function of kinetic diameter, a parameter frequently used to characterize relative penetrant size for light gases.[39] The permeability coefficients of He, H_2, and CO_2 were rather similar, independent of gas size, and higher than those of the other gases considered. The permeabilty of this polymer to O_2, N_2, and CH_4 decreased with increasing penetrant size, consistent with a size sieving mechanism dominating penetrant transport.

The permeability coefficient of gases in polymers is typically expressed as the product of gas solubility and gas diffusivity in the polymer:[26]

$$P_A = S_A D_A$$

where P_A is the permeability coefficient of gas A, S_A is the solubility coefficient of gas A in the polymer, and D_A is the effective, concentration averaged diffusion coefficient of the gas in the polymer. As a result, both solubility and diffusivity contribute to overall permeability characteristics. The ability of a polymer to separate two gases depends on the polymer being more permeable to one gas than the other. In this regard, the ideal separation factor, or selectivity, $\alpha_{A/B}$, is defined as follows:[26]

$$\alpha_{A/B} = P_A/P_B = (S_A/S_B)(D_A/D_B)$$

where P_B is the permeability of the less permeable gas, and S_B and D_B are the solubility coefficient and diffusion coefficient of this gas in the polymer.

The permeability coefficient of carbon dioxide in this polymer was essentially the same as that of hydrogen, despite the larger size of CO_2. This result is unusual. Typically, polymers that are as permeable or more permeable to CO_2 than to H_2 are either rubbery polymers or ultrahigh free volume, disubstituted polyacetylenes, such as PTMSP.[40−42] Both classes of these polymers have a very weak size sieving ability (i.e., diffusion coefficients decrease only modestly with increasing penetrant size).[43] Therefore, the natural tendency for CO_2 to be more soluble in polymers than H_2 (resulting from the more condensable nature of CO_2) is only partially offset by the slightly lower CO_2 diffusion coefficient, resulting in polymers that are more permeable to CO_2 than to H_2.[43] Similary, methane is larger than nitrogen but is more soluble than nitrogen, and as a result, in such weakly size-sieving polymers, methane is more permeable than N_2.[40,42] This is not the case for the polymer considered in this study, since it is more permeable to N_2 than to CH_4.

Table 4. Separation Factors of Poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]]

	Robeson's parameters[a]				separation factors[b]	
	k			P_i		
gas pair	[barrers]	n	gas$_i$	[barrers]	exp	calc
H_2/N_2	52 918	−1.5275	H_2	470	11	22
H_2/O_2	35 760	−2.2770	H_2	470	3.9	6.7
H_2/CH_4	18 500	−1.2112	H_2	470	14	21
O_2/N_2	389 224	−5.8000	O_2	120	2.9	4.0
CO_2/CH_4	1 073 700	−2.6264	CO_2	470	14	19

[a] Data from: Robeson, L. M. *J. Membr. Sci.* **1991,** *62,* 165. [b] Separation factor = $(P_i/k)^{1/n}$.

These composite results suggest that the polymer matrix has a stronger ability to sieve penetrant molecules based on size than the rubbery polymers or ultrahigh free volume disubstituted polyacetylenes mentioned above but that this characteristic is offset by a higher than usual CO_2 solubility. High carbon dioxide solubility (relative to other gases) has been reported for other organic polymers having high concentrations of accessible fluorine groups. Examples include organopolysiloxanes bearing fluorinated side chains and poly(bis(trifluoroethoxy)phosphazene).[44,45] These authors suggest that favorable interactions between fluorinated units in the polymer and carbon dioxide contribute to high CO_2 solubility. In this regard, the trifluoromethyl groups in this polymer may interact favorably with carbon dioxide, which would enhance the permeability coefficient of this polymer to CO_2. More detailed solubility and diffusivity studies, which are beyond the scope of this report, would be required to verify this hypothesis.

Separation factors of several industrial gas pairs are summarized in Table 4. On the basis of an exhaustive search of the polymer permeation literature, Robeson reported that the best combinations of permeability and selectivity obeyed a tradeoff rule: more permeable polymers are less selective and vice versa.[46] Polymers that have permeability and selectivity combinations beyond the so-called upper bound limits identified by Robeson are extremely rare. Robeson reported quantitative relations between gas permeability and selectivity for many common gas pairs. On the basis of the measured permeability coefficients in this polymer, estimates of the selectivity of a hypothetical upper bound polymer with the same permeability coefficients were computed using the relations published by Robeson. These estimated selectivity values are also listed in Table 4 along with the selectivity values determined from the ratios of experimentally determined, pure gas permeability coefficients. All of the separation factors calculated on the basis of the experimental permeability coefficients were lower than their calculated upper bound values. For example, the separation factors of oxygen over nitrogen and carbon dioxide and methane were 2.9 and 13.8, respectively. These values were 73% of their calculated upper bound values and are closer to the upper bound selectivity values than those of the other gas pairs.

As indicated in Table 2, Kapton (an aromatic polyimide) has similar flammability characteristics to PDTFE. However, aromatic polyimides are usually much less permeable to gases than PDTFE. For example, conventional amorphous polyimides exhibit oxygen permeability coefficients of 0.4−16 barrers and O_2/N_2 selectivity values of 4.7−8.3.[21] The O_2 permeability coefficient of PDTFE is 7.5−300 times larger than that of these conventional, thermally stable polyimides, and the O_2/N_2 selectivity values are 35−62% of the values observed for the polyimides. Given the excellent thermal stability of the polymer and its separation properties, which are near the upper bound limits for some gas pairs, this polymer might be of interest as a high-temperature membrane material.

Conclusions

Poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]] was successfully prepared by the nickel-catalyzed carbon−carbon coupling reaction of 2,2-bis(*p*-chlorophenyl)hexafluoropropane. The polymer exhibits excellent thermal and thermooxidative stability. The combination of the thermal stability, minimal moisture absorption, and low dielectric constant indicates that this material and its analogues are promising for electronic applications. The fire resistance testing shows that this new polymer is comparable with other polymers in its class and exceeds present FAA standards. PDTFE has a high free volume and is very gas permeable for an aromatic, glassy polymer. Selectivity values for some gas pairs (O_2/N_2 and CO_2/CH_4) are near the upper bound limits suggested by Robeson. The initial gas permeability measurements suggest a high affinity for carbon dioxide relative to the other gases. Currently, other fluorinated polymers of similar structures are being synthesized and characterized.

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