

Polyesters, Polycarbonate, and Polyurethanes from a Novel Monomer: $\alpha,\alpha,\alpha',\alpha'$ -Tetramethyl-1,4-tetrafluorobenzenedimethanol

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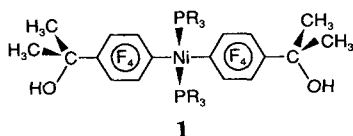
SYNOPSIS

The novel diol monomer, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-tetrafluorobenzenedimethanol, has been synthesized by a convenient route which involves the addition of acetone to 1,4-dilithiotetrafluorobenzene and can be purified by washing with hexanes. It does not directly undergo condensation polymerizations with diacid chlorides. Its disodium salt, prepared by its reaction with sodium hydride, similarly fails to undergo such polymerizations readily. However, the dilithium salt, prepared *in situ* by the reaction of the title diol with 2 equiv of *n*-butyllithium in tetrahydrofuran, is suitable for the preparation of various classes of condensation polymers. Four polyesters and one polycarbonate derived from the reactions of the dilithium salt of the diol with adipoyl dichloride, sebacoyl dichloride, isophthaloyl dichloride, terephthaloyl dichloride, and phosgene and two polyurethanes derived from its reactions with tolylene-2,4-diisocyanate and methylene-di-1,4-phenyl diisocyanate were prepared. Each was fully characterized by GPC, NMR, IR, and UV-visible spectroscopies, and the results of these studies are reported herein. © 1993 John Wiley & Sons, Inc.

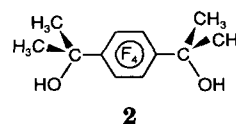
Keywords: tetrafluorobenzene derivatives • fluorinated polymers • condensation polymers • polyesters • polycarbonates • polyurethanes

INTRODUCTION

As part of our ongoing studies of new polymeric materials, we recently reported a series of novel organometallic oligomers and polymers having $\text{Ni}(\text{PMePh}_2)_2$ fragments and fluoroaromatic (e.g., 1,4- C_6F_4 and 4,4'- C_{12}F_8) bridging units in the polymer backbone (e.g., $[\text{Ni}(\text{PMePh}_2)_2]_3(\mu\text{-1,4-C}_6\text{F}_4)_2\text{Br}_2$ and $[\text{Ni}(\text{PMePh}_2)_2(\mu\text{-4,4'-C}_{12}\text{F}_8)]_n$).^{1,2} We are currently extending these studies by investigating more conventional condensation polymers derived from organometallic monomers such as *trans*- $\text{Ni}(\text{PR}_3)_2(1,4\text{-C}_6\text{F}_4\text{CMe}_2\text{OH})_2$, **1**.³

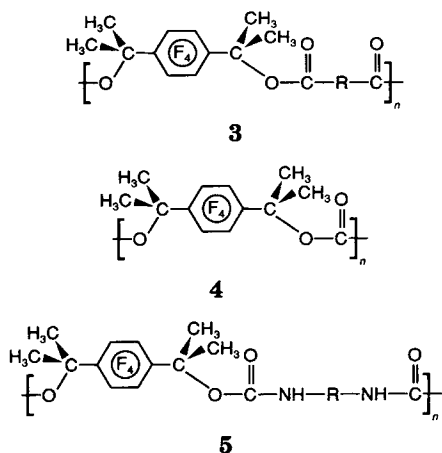


Unfortunately, our early efforts to use this monomer directly in producing polyesters, polycarbonates, and polyurethanes were unsuccessful, probably due to the low nucleophilicity and high steric hindrance of this tertiary alcohol. To identify the origin of this synthetic problem and to find superior routes for such polymerizations, we decided to investigate the chemistry of the most closely related organic monomer, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-tetrafluorobenzenedimethanol, **2**.



Since this compound had not previously been reported, we decided to prepare monomer **2** and use it to study the polymerization conditions required to successfully prepare the $-\text{C}(\text{CH}_3)_2\text{O}-\text{C}(\text{O})-$, $-\text{C}(\text{CH}_3)_2\text{O}-\text{C}(\text{O})-\text{O}-$, and $-\text{C}(\text{CH}_3)_2\text{O}-\text{C}(\text{O})-\text{NH}-$ linkages of polymers having fluoroaromatic bridging units in their backbones.

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We expect that the complete characterization of such purely organic condensation polymers will also serve as an invaluable aid in the identification of their organometallic analogues (i.e., derived from monomer **1**). Further, comparison of the analogous organic and organometallic condensation polymers should help to elucidate the effects of inserting $\text{Ni}(\text{PR}_3)_2$ centers into polymer backbones. In this article, we report the convenient preparation and facile purification of diol **2** and the preparation and characterization of several classes of condensation polymers derived from this novel monomer including polyesters, polycarbonates, and polyurethanes.

EXPERIMENTAL

Materials

1,4-Dibromotetrafluorobenzene, *n*-butyllithium (1.6M in hexanes), dimethyl adipate, adipoyl dichloride, sebacoyl dichloride, isophthaloyl dichloride, and terephthaloyl dichloride were purchased from Aldrich. Phosgene [20% (1.93M) in toluene] was purchased from Fluka. Toluene-2,4-diisocyanate (TDI) and methylene-di-1,4-phenyl diisocyanate (MDI) were purchased from Kodak. All chemicals purchased were of reagent grade and were used without further purification.

Preparation of $\alpha,\alpha,\alpha',\alpha'$ -Tetramethyl-1,4-tetrafluorobenzenedimethanol, **2**

The reaction was conducted using conventional techniques for the manipulation of air-sensitive compounds as described previously.⁴⁻⁷ Thus, anaerobic and anhydrous conditions were maintained by using a prepurified argon or dinitrogen atmosphere employing conventional vacuum line techniques.

Diethyl ether was dried and distilled from $\text{Na}[\text{Ph}_2\text{CO}]$ and stored under Ar or N_2 . Reagent acetone was dried and distilled twice from CaSO_4 (Drierite) and stored under N_2 in the dark. *n*-Butyllithium/hexanes solutions were standardized before use.⁸

1,4-Dibromotetrafluorobenzene (10.0 g, 32.5 mmol) was placed in a 300 mL three-necked flask, followed by introduction of diethyl ether (200 mL). The flask was cooled to -78°C (solid CO_2 /acetone bath) and *n*-butyllithium (1.6M in hexanes, 41.6 mL, 67 mmol) was added dropwise over a period of 15 min. The resulting yellow-white slurry was stirred at -78°C for a further 20 min, and then anhydrous acetone (7.2 mL, 98 mmol) was added dropwise over a period of 5–10 min. Both additions were accompanied by efficient stirring. The resulting white slurry was stirred at -78°C for 15 min and then allowed to warm to ambient temperature ($\approx 23^\circ\text{C}$). The subsequent manipulations were performed in air. The slurry was acidified (pH = 4–6) with hydrochloric acid, and then washed with water until a neutral pH for the aqueous layer was observed. The ether solution was concentrated under vacuum to ≈ 20 mL and hexanes (200 mL) was added to complete the precipitation. The final white crystalline solid was placed in a filter funnel and washed with copious amount of water, followed by hexanes, and then allowed to air-dry for 2 h. The solid was then redissolved in tetrahydrofuran (30 mL), and reprecipitated by the addition of hexanes (300 mL). Product **2** was collected by filtration and air-dried overnight in 67% yield (5.8 g). mp $157\text{--}159^\circ\text{C}$. $^1\text{H-NMR}$ (CD_2Cl_2): δ 1.72 (m, 12H), δ 2.74 (s, br, 2H). $^{19}\text{F-NMR}$ (CD_2Cl_2): δ -142.01 (s). Low resolution mass spectrum: 266 (P^+), 251 ($\text{P}^+ - \text{CH}_3$).

ANAL. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_4\text{O}_2$. C, 54.14%; H, 5.30%. Found: C, 54.23%; H, 5.39%.

Polymerization

Representative examples of the preparations of the new polyesters, polycarbonate and polyurethanes prepared in this work are given below. Details of yields and characterization data are given in Tables I–III. All polymerizations were conducted under an atmosphere of dry N_2 .

Polyester from Sebacoyl Dichloride

To a solution of the diol **2** (0.500 g, 1.88 mmol) in tetrahydrofuran (40 mL) cooled to 0°C (ice/water bath) was added dropwise *n*-butyllithium (1.6M in

Table I. Yield, Molecular Weight, and Melting Point Data

Reactant	Polymer	Yield (%)	VPO Molecular Weight ^a	GPC Molecular Weight ^b		[η] ^c (dL/g)	Melting Point ^d (°C)
				\bar{M}_n	\bar{M}_w		
Sebacoyl dichloride	3a	37	4892	4460	7260	0.11	72–96
Adipoyl dichloride	3b	62	682	1100	1850	0.057	— ^e
Isophthaloyl dichloride	3c	95	1843	1900	3950	0.082	110–148
Terephthaloyl dichloride	3d	95	—	—	—	—	240–250
Phosgene	4a	96	1082	1000	2200	0.055	118–196
Tolylene-2,4-diisocyanate	5a	51	—	—	—	0.057	176–dec
Methylene-di- <i>p</i> -phenyl diisocyanate	5b	89	—	—	—	0.11	290–dec

^a Number-average molecular weight, \bar{M}_n .^b Molecular weights are relative to polystyrene.^c Measured in THF at 30°C except for **5a** and **5b** where [η] is measured in DMF at 30°C.^d Range from initiation of melting to completely molten.^e Liquid at room temperature.

hexanes, 2.46 mL, 3.9 mmol), producing the presumed $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-tetrafluorobenzene dimethoxydilithium **2Li**. The resulting white slurry was stirred at 0°C for 30 min and then sebacoyl dichloride (0.400 mL, 1.88 mmol) was added dropwise. The clear yellow solution produced was stirred at 0°C for 10 min, then at ambient temperature for 18 h. The solvent was reduced in volume under vacuum to ≈ 10 mL and the flask was cooled to 0°C, at which point methanolic hydrochloric acid was added and the pH adjusted to 4–6. The mixture was then poured into H₂O (200 mL), warmed to $\approx 60^\circ\text{C}$ with stirring, and subsequently filtered. The solid was washed with excess water and hexanes (3 \times 20 mL) and air-dried overnight, yielding 37% (0.30 g) of pale yellow powder of **3a** ($-\text{[OC(CH}_3)_2\text{C}_6\text{F}_4\text{C(CH}_3)_2\text{OC(O)(CH}_2)_8\text{C(O)-}]_n-$).

Polycarbonate from Phosgene

A slurry of the dilithium salt of the diol, **2Li** (1.88 mmol), in tetrahydrofuran (40 mL) was prepared at 0°C as described above. To this mixture, was added dropwise phosgene (1.93 M in toluene, 1.00 mL, 1.93 mmol). The resulting yellow solution was stirred at 0°C for 10 min, then at ambient temperature for 18 h. The solution was concentrated under vacuum to ≈ 10 mL and cooled to 0°C, after which it was poured into water (200 mL) and the pH adjusted to 4–6. The mixture was then warmed to $\approx 60^\circ\text{C}$ with stirring and subsequently filtered. The final pale yellow powder was washed with excess water and hexanes (2 \times 10 mL) and air-dried

overnight, giving 96% (0.55 g) yield of **4a** ($-\text{[OC(CH}_3)_2\text{C}_6\text{F}_4\text{C(CH}_3)_2\text{OC(O)-}]_n-$).

Polyurethane from MDI

A solution of the diol **2** (0.500 g, 1.88 mmol) in dimethyl sulfoxide (10 mL) and pyridine (1.0 mL, 12 mmol) was placed in a three-necked flask equipped with a magnetic stirrer and an air-condenser. MDI (0.470 g, 1.88 mmol) was added, and the solution was heated to reflux and this temperature was maintained for a further 7 h. The clear viscous brown solution was cooled to ambient temperature and poured into water (400 mL). The mixture was warmed to $\approx 80^\circ\text{C}$ with stirring and subsequently filtered. The polymer was washed with excess water, followed by hexanes, and air-dried overnight, giving a very fine, tan-colored powder in 89% (0.86 g) yield of **5a** ($-\text{[OC(CH}_3)_2\text{C}_6\text{F}_4\text{C(CH}_3)_2\text{OC(O)NH-1,3-(4-CH}_3)_3\text{C}_6\text{H}_3\text{NHC(O)-}]_n-$).

Attempted Preparation of Polyester from Diol 2 and Sebacoyl Dichloride by Solution Polymerization

To a solution of the diol **2** (0.500 g, 1.88 mmol) and pyridine (0.5 mL, 6 mmol) in dichloromethane (50 mL) was added sebacoyl dichloride (0.400 mL, 1.88 mmol) dropwise with stirring. The resulting clear solution was stirred at ambient temperature ($\approx 23^\circ\text{C}$) for 10 h, and then refluxed for another 10 h. A sample was taken whose GPC in tetrahydrofuran revealed that only low oligomers of the polysebacate were obtained ($\overline{\text{DP}}_n \approx 3$).

Table II. ^1H - and ^{19}F -NMR Assignment^a

Polymer	Primary Structure ^b	^1H (ppm)	^{19}F (ppm)
3a	$-\text{[} -\text{OC}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{C}(\text{CH}_3)_2\text{OC}(\text{O})(\text{CH}_2)_8\text{C}(\text{O}) - \text{]}_n -$	2.28 (t, $^3J_{\text{H-H}} = 7.54 \text{ Hz}$, 4H, $\underline{\text{H}_\alpha}$), 1.80 (s, $\underline{\text{CH}_3}$), 1.57 (m 4H, $\underline{\text{H}_\beta}$), 1.29 (br, 8H, $\underline{\text{H}_\gamma}$ and $\underline{\text{H}_\delta}$)	-141.97 (s, br)
3b	$-\text{[} -\text{OC}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{C}(\text{CH}_3)_2\text{OC}(\text{O})(\text{CH}_2)_4\text{C}(\text{O}) - \text{]}_n -$	2.31 (br, 4H, $\underline{\text{H}_\alpha}$), 1.80 (s, $\underline{\text{CH}_3}$), 1.59 (m, 4H, $\underline{\text{H}_\beta}$)	-141.92 to -141.99 (br)
3c	$-\text{[} -\text{OC}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{C}(\text{CH}_3)_2\text{OC}(\text{O})-1,3-\text{C}_6\text{H}_4\text{CO} - \text{]}_n -$	8.60 (m, $\underline{\text{ArH}}$), 8.20 (m, $\underline{\text{ArH}}$), 7.54 (m, $\underline{\text{ArH}}$), 1.97 (s, br, $\underline{\text{CH}_3}$)	-140.95 to -141.30 (br)
3d	$-\text{[} -\text{OC}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{C}(\text{CH}_3)_2\text{OC}(\text{O})-1,4-\text{C}_6\text{H}_4\text{C}(\text{O}) - \text{]}_n -^c$	8.07 (m, $\underline{\text{ArH}}$), 1.98 (s, br, $\underline{\text{CH}_3}$)	-139.74 to -141.65 (m)
4a	$-\text{[} -\text{OC}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{C}(\text{CH}_3)_2\text{OC}(\text{O}) - \text{]}_n -$	1.78 (s, br, $\underline{\text{CH}_3}$)	-141.95 (s, br)
5a	$-\text{[} -\text{OC}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{C}(\text{CH}_3)_2\text{OC}(\text{O})\text{NH}-1,3-(2-\text{CH}_3)\text{C}_6\text{H}_3\text{NHC}(\text{O}) - \text{]}_n -$	9.66 (br, $\underline{\text{NH}}$), 8.94 (m, br, $\underline{\text{NH}}$), 8.65-7.60 (m, br, $\underline{\text{ArH}}$), 7.39-6.90 (m, $\underline{\text{ArH}}$), 2.17 (m, br, $\underline{\text{ArCH}_3}$), 1.84 (s, br, $\underline{\text{CH}_3}$)	-139.73 to -144.17 (m)
5b	$-\text{[} -\text{OC}(\text{CH}_3)_2\text{C}_6\text{F}_4\text{C}(\text{CH}_3)_2\text{OC}(\text{O})\text{NHC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHC}(\text{O}) - \text{]}_n -$	9.69 (br, $\underline{\text{NH}}$), 8.52 (br, $\underline{\text{NH}}$), 7.32 (m, $\underline{\text{ArH}}$), 7.06 (m, $\underline{\text{ArH}}$), 3.76 (m, br, $\underline{\text{CH}_2}$), 1.83 (s, br, $\underline{\text{CH}_3}$)	-139.69 to -144.16 (m)

^a Dichloromethane- d_2 as the solvent except for **5a** and **5b** where dimethyl sulfoxide- d_6 was used as the solvent.^b Unspecified phenylenes denote para linkages.^c Dichloromethane- d_2 soluble portion (< 10% by weight).

Table III. UV-Visible and Infrared Absorption Data

Polymer	UV Maxima (nm)	IR Frequencies ^a (cm ⁻¹)			
		C—F	C=O	C—O	N—H
3a	240 (m), 264 (s), 290 (w)	1132	1738	1292	—
3b	246 (s), 260 (s), 290 (w)	1131	1737	1292	—
				1251	
3c	240 (s), 264 (m), 290 (w)	1135	1726	1293	—
3d	248 (vs), 294 (w) ^b	1101–1116	1720	1280	—
		1143			
4a	240 (m), 264 (vs), 290 (w)	1123	1747	1287	—
5a	250 (vs), 294 (m) ^b	1140	1685 (br)	1228	1536 (br); 3100–3600
5b	250 (vs), 294 (m) ^b	1139	1712 (br)	1233	1511–1524 1596; 3100–3600

^a Measured as dichloromethane casts except for **3d**, **5a**, and **5b** where the spectra were recorded as KBr pellets.

^b THF soluble portion (< 10% by weight).

Attempted Preparation of Polyester from Diol 2 and Sebacoyl Dichloride by Melt Polymerization

The diol **2** (1.00 g, 3.76 mmol) and sebacoyl dichloride (0.800 mL, 3.75 mmol) were placed in a three-necked flask equipped with a N₂ gas inlet extending beneath the reaction mixture and an air condenser with a gas outlet on top. The mixture was heated to 120°C (silicon oil bath), at which time the reaction started and a viscous liquid was formed with hydrochloric acid gas smoke filling the flask. A gentle stream of N₂ was applied and the mixture was heated for a few hours during which the temperature of the heating source was gradually raised to 150°C. Deposits of the diol (revealed by its GPC and UV absorption) were observed on the inner wall of the condenser. Heating was stopped when the mixture became colored. GPC showed the polysebacate obtained was only low oligomers ($\overline{DP}_n \approx 3$).

Attempted Preparation of Polyester from 2Na and Sebacoyl Dichloride

The diol **2** (1.00 g, 3.76 mmol) and sodium hydride (60% dispersion, 0.39 g, 9.8 mmol) diluted by tetrahydrofuran (50 mL) were placed in a three-necked flask equipped with a magnetic stirrer and an air condenser. The mixture was refluxed for 2.5 h, and the presumed disodium salt of the diol, **2Na** thus formed.⁹ At this point sebacoyl dichloride (0.800 mL, 3.75 mmol) was added dropwise. An exotherm was observed and an orange-yellow voluminous precipitate was formed. The mixture was refluxed for 4 h, then its solvent was replaced by *N,N*-dimethyl acetamide (30 mL) and refluxed for 10 h. The solvent was reduced in volume by vacuum to ≈ 10 mL and

the flask cooled to room temperature. Methanol (2 mL) was added and stirred for ≈ 2 min, followed by addition of water (50 mL) and the pH of the mixture was adjusted to pH ≈ 4 . A sticky dark brown solid was obtained after filtration of the mixture and washing with excess water. The solid was air-dried overnight, giving 62% (1.0 g) yield. GPC showed the polysebacate obtained had $\overline{M}_n = 1620$, $\overline{M}_w = 3580$ (relative to polystyrene). This polymer gradually loses its solubility in solvents in days under ambient conditions. Its ¹⁹F-NMR spectrum exhibited complicated resonances and differential scanning calorimetry (DSC) showed no clear thermal transformations until decomposition.

¹H-NMR Data of the Model Compounds

Dimethyl sebacate (**6a**), (2-methyl-1,3-phenylene), bisdimethyl carbamate (**7a**), and (methylenedi-1,4-phenylene)bisdimethyl carbamate (**7b**) were prepared via the reactions with excess anhydrous methanol, of sebacoyl dichloride, TDI, and MDI, respectively. Reactions were achieved by refluxing methanol for 2–4 h and the yields were quantitative. Triethylamine was used as the base in the preparation of **6a**. Dimethyl adipate (**6b**) was used as purchased.

¹H-NMR (CD₂Cl₂) for **6a**: δ 2.27 (t, ³J_{H-H} = 7.54 Hz, 4H, H_a), 1.58 (m, 4H, H_b), 1.29 (br, 8H, H_c and H_d).

¹H-NMR (CD₂Cl₂) for **6b**: δ 2.27 (br, 4H, H_a), 1.58 (m, 4H, H_b).

¹H-NMR [(CD₃)₂SO] for **7a**: δ 9.53 (s, br, 1H, NH), 8.80 (s, br, 1H, NH), 7.47 (s, 1H, ArH), 7.15 (dd, 1H, ArH), 7.05 (d, 1H, ArH), 2.10 (s, 3H, ArCH₃).

$^1\text{H-NMR}$ [$(\text{CD}_3)_2\text{SO}$] for **7b**: δ 9.53 (s, br, 2H, NH), 7.32 (d, 4H, ArH), 7.08 (d, 4H, ArH), 3.77 (s, 2H, CH_2).

Measurements

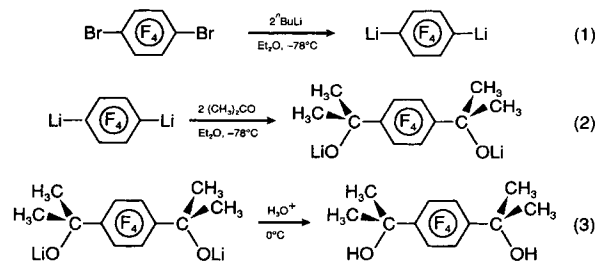
The NMR spectra were recorded on a Bruker AM-400 spectrometer as dichloromethane- d_2 (CD_2Cl_2) or dimethyl sulfoxide- d_6 [$(\text{CD}_3)_2\text{SO}$] solutions and employing a deuterium solvent lock. The $^{19}\text{F-NMR}$ chemical shifts are reported in parts per million downfield from external CFCl_3 and the $^1\text{H-NMR}$ chemical shifts downfield from external Me_4Si . The IR spectra were recorded on a Nicolet 7199 spectrophotometer. Melting points were ascertained by visual methods in unsealed capillaries. Osmometry measurements were made in benzene solutions on a Corona Wescan Vapor Pressure Osmometer by the University of Alberta Microanalytical Services. Gel permeation chromatography was performed on an automated Waters 600E HPLC/GPC system operated at 30.0°C using tetrahydrofuran as the eluting solvent at a flow rate of 1.20 mL/min through three Waters HT μ -Styragel columns (10^3 Å, 10^6 Å, and $10\ \mu\text{m}$ linear). Chromatograms and UV-visible spectra were collected on-line on a Waters 991 Photodiode Array (UV-visible) detector incorporating a Waters 410 Differential Refractive Index detector. Molecular weight calculations were performed using the Maxima 820 chromatography software (Waters, Dynamic Solutions, Division of Millipore) based on calibration using polystyrene narrow standards. Intrinsic viscosities were measured in 0.05–0.1% solutions using an Ubbelohde viscometer in a water bath maintained at $30 \pm 0.01^\circ\text{C}$ and calculated according to the method described by Solomon and Ciuta.¹⁰

RESULTS AND DISCUSSIONS

Preparation of the Diol Monomer

One of the criteria for the practical application of a new bifunctional monomer in condensation polymerizations is that the monomer be readily accessible and of high purity since impurities such as monofunctional species will upset the balance of stoichiometry and prevent the formation of high molecular weight polymers. It is in this context that we report preparation of the novel diol monomer since it offers the advantage of convenient synthesis and facile purification, and is therefore suitable for preparations of various classes of condensation

polymers. Bromine–lithium exchange between 1 equiv of 1,4-dibromotetrafluorobenzene and 2 equiv of *n*-butyllithium produces 1,4- $\text{C}_6\text{F}_4\text{Li}_2$.^{1,2,11–16} When this is followed by derivatization using 2 equiv of acetone, the desired diol **2** is produced in high yield and in multigram quantities [eqs. (1)–(3)]:



It was found that solvent played a critical role in the synthesis. In particular, an isolated yield of 80% could be achieved when diethyl ether was used as the solvent, while less than 30% was obtained when tetrahydrofuran (THF) was employed. This is presumably due to the acidity of the α -hydrogen atoms of acetone^{17,18} and the greater basicity of the perfluoroaryl dilithium reagent in THF. Elimination of lithium fluoride to form benzene derivatives during the preparation of the aryl dilithium can occur on scaling up this exothermic reaction.^{12–16} This may be avoided or minimized by slow addition of *n*-butyllithium/hexanes solutions. This product is simple to purify and its analytical and spectroscopic data show that it is essentially 100% pure after washing with hexanes and reprecipitation from THF/hexanes (see Experimental section), since the monofunctional by-products and other impurities are very soluble in hexanes while the diol is not. In fact, transparent colorless needle-like crystals can be easily grown from diethyl ether or dichloromethane solutions. The diol is readily soluble in THF, acetone, and ethanol and is moderately soluble in diethyl ether, dichloromethane, and chloroform.

Preparation of Condensation Polymers

Four polyesters, one polycarbonate, and two polyurethanes have been prepared using the novel diol monomer **2** employing modified solution polymerization techniques. These polymers were characterized using vapor pressure osmometry (VPO) and gel permeation chromatography (GPC) for determinations of molecular weights, and $^1\text{H-}$ and $^{19}\text{F-NMR}$, IR, and UV-visible spectroscopies for determinations of primary structures. These data are listed in Tables I–III. Since it is easier to obtain and interpret the spectroscopic, particularly NMR data,

at the relatively low molecular weight level, no attempt was made to maximize the molecular weights of the polymers.

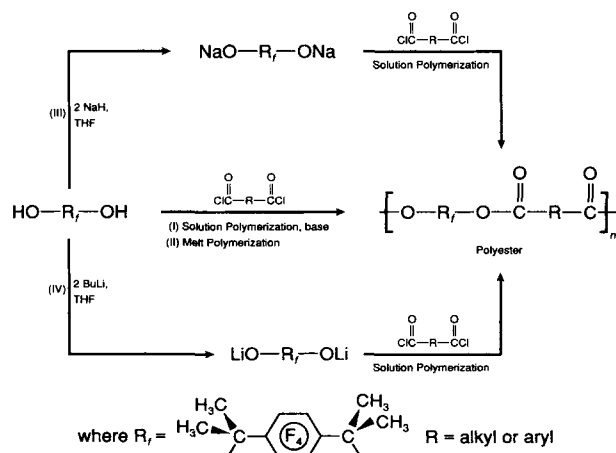
Preparation and Characterization of Polyesters 3a–3d and Polycarbonate 4a

Four different routes leading from the diol monomer **2** to the polyesters have been attempted (Scheme 1). The first route involves the direct polymerization of the diol with diacid chlorides in solution (Schotten–Baumann reactions) using pyridine or triethylamine as the base. Although the mixture was found to be completely soluble in certain solvents such as dichloromethane or chloroform, only low oligomers were produced through this procedure even at elevated temperatures. This is probably due to the relatively low nucleophilicity and high steric hindrance expected of the tertiary alcohol. The volatility of the diol seems to have prevented the success of melt polymerization due to resultant nonoptimal stoichiometry in our open reaction system, while prolonged heating of the reaction mixture above 120°C resulted in decomposition of the oligomers formed. Although conversion to the disodium salt of the diol, **2Na**, was relatively easy to achieve in THF,⁹ the reaction mixture remained insoluble in this solvent after addition of diacid chloride even at refluxing temperature; thus, heating in *N,N*-dimethyl acetamide (bp ≈ 165°C) was necessary to effect the further conversion of the oligomers formed in THF into higher molecular weight species. For this monomer, polymers of acceptable molecular weight were obtained after a few hours of heating. Unfortunately, the products isolated were dark brown colored and decomposed spontaneously in air at ambient temperature, their ¹⁹F NMR spectra were also

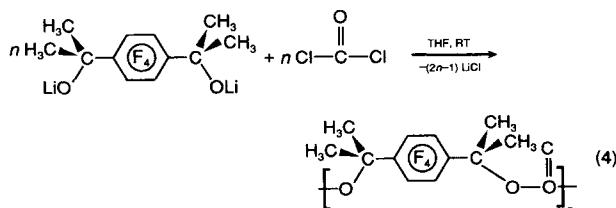
unexpectedly complicated. Therefore, the above three routes were not further investigated. The fourth route, involving the dilithium salt, **2Li**, however, was found to be successful. It produced a solution that was totally clear upon addition of diacid chlorides into the dilithium salt suspension of **2Li** in THF (except for the case of polyterephthalate whose reaction mixture precipitated out of the solution). Although the conditions for this transformation have not been optimized, the polymerization under the conditions described could be completed in a few hours at ambient temperature and polyesters of acceptable molecular weights were obtained. Therefore, this route was chosen to prepare the four polyesters reported (i.e., polysebacate, **3a**, polyadipate, **3b**, polyisophthalate, **3c**, and polyterephthalate, **3d**).

Except for the polyterephthalate, **3d**, which is only sparingly soluble, these polyesters are readily soluble in common solvents, such as THF, acetone, dichloromethane, and benzene, which aids in their subsequent characterizations. Interestingly, but not surprisingly, the GPC results for molecular weight measurement are consistent with the osmometry data (Table I), even though the molecular weights reported from GPC are calculated according to polystyrene. The spectroscopic data for these polymers suggest that they possess the expected primary structures. In particular, the ¹H- and ¹⁹F-NMR resonances are completely assigned (see Table II) by comparison to some model compounds, although peak broadening was encountered in some cases (presumably due to the polydisperse nature of the polymers). The IR absorptions of the polymers are consistent with the assigned structures, and typical frequencies due to C=O, C—O, and C—F listed in Table III indicate the integrity of “ester” linkages derived from reactions between the diacid chlorides and the diol. The UV absorptions of these polymers are also consistent with this suggestion. Thus, they normally show a strong shoulder absorption between 240 and 260 nm (Table III), presumably arising from the arene ring and the carbonyl $\pi \rightarrow \pi^*$ transitions, together with a weak maxima at ca. 290 nm.

The polycarbonate, **4a**, was prepared via the same route as that used for the polyesters [eq. (4)]:



Scheme 1.

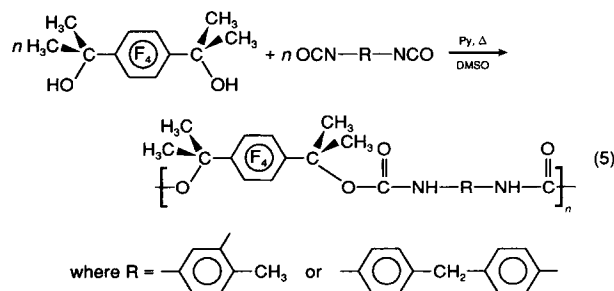


In fact, the polycarbonate should possess a primary structure similar to that of the polyesters and therefore should be expected to have similar properties. Indeed, its simple ^1H - and ^{19}F -NMR data (Table II) revealed the expected structure, the identity of which is further supported by its IR and UV absorptions (Table III). Similar to the polyester analogues, the polycarbonate is readily soluble in most common solvents.

These polyesters and polycarbonate normally melt between ambient temperature and 250°C , low initial temperatures of **3a–3c** and **4a** indicate the presence of lower oligomers (Table I). As expected, the polyarylates possess higher melting ranges than the polyalkylates, reflecting the greater chain stiffness or higher crystallinity when arene bridges are introduced into the polymer backbone. The polyterephthalate, **3d**, shows the highest and narrowest melting range (240 – 250°C), suggesting the possibility of the very high crystallinity expected for a highly symmetrical backbone. However, we are unable to obtain its molecular weight data due to its poor solubility characteristics.

Preparation and Characterization of Polyurethanes

Considering the possible lower reactivity of the tertiary diol, **2**, Lyman's method for making polyurethanes¹⁹ was modified by incorporating pyridine (a tertiary amine) as the catalyst. As a result, two polyurethanes were successfully made through this convenient solution technique [eq. (5)]:



These polyurethanes are essentially insoluble in common solvents such as THF and dichloromethane etc., they are, however, soluble in highly polar solvents such as dimethyl sulfoxide (DMSO) and *N,N*-dimethyl formamide (DMF), and intrinsic viscosities are therefore reported (Table I). In contrast to the polyesters and polycarbonate, the polyurethanes do not show a clear melting range. Rather, they begin to shrink before they decompose. These

polymers appear very hard and brittle at ambient temperature.

Dimethyl sulfoxide was used as the solvent to collect the NMR data of the polyurethanes (Table II). In contrast to the NMR spectra of the polyesters and the polycarbonate which are relatively simple, those for the polyurethanes show broader peaks in the ^1H -NMR and multiplets in the ^{19}F -NMR spectra. However, with the aid of some model compounds, tentative assignments can be made which suggest the polyurethanes possess the expected primary structures. IR data for these polymers (Table III) are also in accord with this suggestion. Thus, distinctive and strong absorptions due to N-H , C-F , and $-\text{C}(\text{O})-\text{O}-$ groups can be readily identified from the spectra, the amide carbonyl stretching frequencies being considerably lower (by 30 – 50 cm^{-1}) than those of the ester carbonyls. The UV spectra of these polyurethanes show two maxima, namely a strong absorption at 250 nm and a medium absorption at 294 nm .

In conclusion, acetone derivatization of dilithio-tetrafluorobenzene afforded a high purity bifunctional monomer which was found to be suitable for the preparation of various classes of condensation polymers. Although in these small scale preparations, relatively low molecular weight polymers were obtained, we expect high polymers would be accessible upon scaling up the reactions. These results suggest improved routes to the analogous organometallic condensation polymers. Work is underway to extend this methodology and to optimize the polymerization conditions which can be applied to the preparation of these polymers.

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