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Synthesis and polymerization of trifluorovinylether-terminated imide oligomers. I

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Abstract

The objective of this research was the preparation of imide trimers, terminated with trifluorovinyl ether groups, that could be melt processed and then polymerized to high molecular weight via the thermal dimerization of the trifluorovinyl ether moieties. The work was begun with the synthesis of an aromatic amine end-capping agent containing trifluorovinyl ether functionality, i.e. 4-(trifluorovinyloxy)aniline (TFVA). Melt-processable imide trimers were prepared from the end-capping agent and 2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BisA-DA) and 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA). The trimers underwent thermal cyclopolymerization to afford polyimides containing perfluorocyclobutane (PFCB) rings. The DSC thermogram of the imide trimer prepared from TFVA and BisA-DA contained a melting endotherm with a minimum of 153°C and a polymerization exotherm with a maximum at 220°C. The thermogram of the trimer prepared from TFVA and 6FDA had a melting endotherm with a minimum at 136°C and a polymerization exotherm with a maximum at 244°C. The PFCB-containing polyimides obtained from the melt polymerizations had intrinsic viscosities of 0.63 and 0.31 dl/g, respectively. The TFVA/BisA-DA polymer had a T_g of 186°C, while the T_g of the TFVA/6FDA polyimide was 206°C. The coefficient of thermal expansion of a thin film of the TFVA/BisA-DA polyimide was $57.1 \times 10^{-6} (°C)^{-1}$. The film displayed a tensile strength of 88 MPa, a modulus of 2113 MPa, and elongation at break of 6.5%. The water absorption of this polyimide was 0.08%. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorinated polyimides; Perfluorocyclobutane; Trifluorovinyl ether groups

1. Introduction

Aromatic polyimides (PIs) are known for their exceptional mechanical, thermal, and electrical properties. Because of this unusual combination of properties, they are widely used in high temperature films, adhesives, and molded parts [1]. Since many PIs are insoluble in organic solvents, they are solution processed in the form of their poly(amic acid) precursors, which are then converted in place to the polyimides. This is especially true in the case of film and adhesive applications. Due to their high glass transition temperatures (T_gs), thermoplastic PIs must be melt processed at elevated temperatures, where they often display limited melt flow. Although this has not precluded their use in molding operations, it has limited their utility in microelectronic and composite applications. One of the most successful approaches to improving melt processability has involved the use of monomers and oligomers endcapped with reactive groups that are subsequently polymerized [2]. This approach provides very processable materials with low transition temperatures and good solubilities. The reactive end groups that have been used include maleimides, nadimide, benzocyclobutenes, ethynyl, and phenylethynyl groups [3,4].

The incorporation of fluorine in polymers continues to be important in the development of advanced materials exhibiting high thermal and thermo-oxidative stability, chemical resistance and superior electrical insulating ability [5–7]. A relatively recent focus has involved the synthesis of partially fluorinated polyimides, where placement of fluorine-containing segments or substituents within the repeating unit has been used to enhance properties [8–12]. For example, dielectric constants have been decreased and thermal stability increased without sacrificing and frequently improving processability [8,11,12].

Recently, Babb and coworkers at the Dow Chemical Corporation developed a new synthetic route to fluorine-containing polymers [13]. In this route, monomers and oligomers are prepared that are terminated with trifluorovinyl ether groups. The terminal groups dimerize upon heating at 200–220°C to afford perfluorocyclobutane (PFCB)

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rings. The dimerization provides a controllable, step-growth mode of polymerization without the production of by-products. Polyarylethers [13–17] and polysiloxanes [18–21] containing PFCBs have been prepared by this route. The PFCB-containing polymers have low dielectric constants, good thermal/oxidative stability, excellent processability, and optical transparency. Thus, it was postulated that PFCB-containing polyimides would also display superior properties that would make them especially attractive for microelectronic, optical and composite applications.

The objective of this research was the preparation of imide oligomers end-capped with trifluorovinyl ether groups that could be melt processed and then thermally dimerized to high molecular weight. The work was to begin with the synthesis of the end-capping agent, 4-(trifluorovinyloxy)aniline (TFVA). Aromatic dianhydrides were then to be treated with a greater than 2:1 excess of the end-capping agent to afford the corresponding trimer. The oligomer molecular weight was to be minimized in order to minimize the melt flow temperature and the melt viscosity. The dianhydrides 2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BisA-DA) and 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were to be used because their flexible linkages were also expected to contribute to a minimum flow temperature. A low flow temperature was sought to provide a melt “processing window” prior to the onset of the thermal dimerization of the trifluorovinyl ether groups. The trimers were to be thermally cyclopolymerized to afford PFCB-containing PIs, which were to be thoroughly characterized.

2. Experimental

2.1. Reagents and solvents

Zinc (granular, Aldrich) was activated with 0.1 M hydrochloric acid, washed with water and acetone, and dried at 100°C under reduced pressure for 2 h. *N*-Methyl-2-pyrrolidinone (NMP) and acetonitrile (Aldrich) were distilled under reduced pressure after drying with phosphorous pentoxide (P_2O_5) and magnesium sulfate ($MgSO_4$), respectively. 2,2′-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (Hoechst Celanease Corp.) was dried at 150°C under reduced pressure and sublimated prior to use. 2,2′-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BisA-DA) (General Electric Co.) was recrystallized from acetic anhydride and dried at 150°C under reduced pressure. Isoquinoline (Aldrich) was distilled under reduced pressure prior to use. All of the other reagents and solvents were used as received.

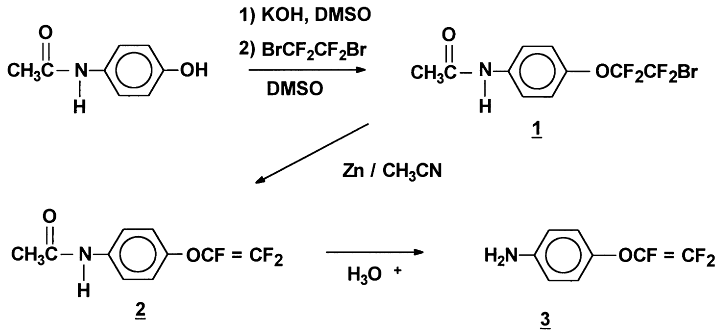
2.2. Instrumentation

Infrared (IR) spectra were obtained with a Mattson Galary Series FTIR 5000 spectrophotometer using neat or film samples. Proton and carbon nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were obtained with a Varian Gemini-200 spectrometer at 200 MHz with tetramethylsilane as the reference. Fluorine nuclear magnetic resonance (^{19}F-NMR) spectra were obtained with a Varian XL-400 spectrometer at 400 MHz with α,α,α-trifluorotoluene as the reference. Intrinsic viscosities were determined on NMP solutions using a Cannon-Ubbelohde No. 100 viscometer at 30.0 ± 0.1°C. Melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Elemental analysis were performed by Galbraith Laboratories, Knoxville, TN. High-pressure liquid chromatogaphy (HPLC) analyses were performed on a Shimadzu Model SPD-6A equipped with a diode array UV (254 mm) detector using a Micropak CH-18 column (30×4 mm^2) with a 60/40 (vol/vol) acetonitrile/water mixture as the eluent. Gel permeation chromatography (GPC) was carried out on a Waters 150-CV equipped with a refractive index detector. Tetrahydrofuran (THF) was used as the elution solvent. Differential scanning calorimetery (DSC) data were obtained on a DuPont Model 2000 in nitrogen using a heating rate of 10°C/min. Thermogravimetric analysis (TGA) data were obtained in nitrogen and air with a TA Hi-Res TGA 2950 thermogavimetric analyzer using a heating rate of 20°C/min. Coefficients of thermal expansion (CTEs) were determined with thermal mechanical analysis (TMA) using a TA TMA 2940 thermomechanical analyzer with a tension mode. Mechanical properties were determined on a Model 1130 Instron® at room temperature.

2.3. Preparation of end-capping agent

2.3.1. 4-(2-Bromotetrafluoroethoxy)acetamidobenzene (**1**)

To a 500-ml, three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a condenser, and a Dean-Stark azeotropic distillation assembly were added 4-acetamidophenol (75.6 g, 0.50 mol), potassium hydroxide (28.1 g, 0.50 mol), 300 ml of dimethyl sulfoxide, and 100 ml of *m*-xylene. The mixture was purged with nitrogen for 30 min, and then heated to 100°C under the reduced pressure (ca. 200 mm Hg) for 48 h, during which time water was removed by distillation. The dry salt solution was cooled to 30°C and 1,2-dibromotetrafluoroethane (129.9 g, 0.55 mol) was added dropwise over 1.5 h with constant cooling with an water bath such that the temperature did not exceed 30°C. The solution was stirred for 12 h at room temperature and then heated for 10 h at 35°C. The reaction mixture was poured into 1 l of water. The product was collected by filtration and washed with water. The product was dissolved in methylene chloride and decolorized with charcoal. The solvent was removed on a rotary evaporator. The light-brown residue was collected by filtration and recrystallized from a mixture of hexane and ethanol to obtain 82.5 g (50%) of white crystals: m.p. 99–101°C; IR (KBr) 3100–3400 (–NH), 3000–3100 (Ar), and 1700 cm^{-1}(C=O); ^{1}H-NMR



Scheme 1.

($CDCl_3$) δ 7.2–7.8 (2d, 4H, Ar–H), 10.1 (s, 1H, NH), and 2.1 ppm (s, 3H, CH_3)

2.3.2. 4-(Trifluorovinyloxy)acetamidobenzene (**2**)

4-(2-Bromotetrafluoroethoxy)acetamidobenzene (30.3 g, 0.092 mol) was slowly added to the solution of activated zinc (6.6 g, 0.10 mol) and 300 ml of acetonitrile in a 500-ml three-necked flask equipped with a reflux condenser, a nitrogen inlet, a thermometer, a mechanical stirrer, and an addition dropping funnel at 80°C. After the mixture was heated at reflux for 12 h, the salt was removed by filtration, and the filtrate was extracted several times with 200 ml of hexane. The extract was evaporated to dryness on a rotary evaporator. The residue was recrystallized from a mixture of hexane and ethanol to obtain 12.76 g (60%) of white crystals. The crystals were chromatographed on a basic alumina column using hexane and ethyl acetate as the eluent to obtain pure white powder: mp 72–73°C, IR (KBr) 1833 ($-CF{=}CF_2$), 3100–3400 (–NH), and 1700 cm^{-1}(C=O); ^{1}H-NMR ($CDCl_3$) δ 6.9–7.5 (2d, 4H, Ar–H), 8.0 (s, 1H, NH), and 2.1 ppm (s, 3H, CH_3); ^{19}F-NMR ($CDCl_3$) δ -119 (1F, dd, *cis*-$CF{=}CF_2$), -126.5 (1F, dd, *trans*-$CF{=}CF_2$), and -136.3 ppm (1F, dd, $-CF{=}CF_2$).

2.3.3. 4-(Trifluorovinyloxy)aniline (TFVA, **3**)

4-(Trifluorovinyloxy)acetamidobenzene (12.76 g, 0.055 mol) was added to a 10% aqueous hydrochloric acid solution, and the solution was stirred and heated at reflux for 2 h. The reaction mixture was allowed to cool to room temperature and neutralized to pH 7 with a 10% aqueous sodium hydroxide solution. The solution was extracted several times with 50 ml of methylene chloride. The combined extracts were washed twice with water, and the solvent was removed on a rotary evaporator to yield 10.98 g (95%) of a very light yellow liquid, which was chloromatographed on a basic alumina column with a mixture of hexane and ethyl acetate as the eluent to give 5.20 g (45%) of a clear liquid: bp 80–85°C/1.0 mmHg; IR (neat) 1834 ($-CF{=}CF_2$), 3100 and 1508 (Ar), and 3300–3500 cm^{-1} (NH_2); ^{1}H-NMR ($CDCl_3$) δ 3.6–3.7 (s, 2H, NH_2), and 6.6–7.0 ppm (2d, 4H, Ar–H); ^{19}F-NMR ($CDCl_3$) δ -121.9 (1F, dd, *cis*-$CF{=}CF_2$), -128.9 (1F, dd, *trans*-$CF{=}CF_2$), and -135.0 ppm(2d, $-CF{=}CF_2$); ^{13}C-NMR ($CDCl_3$) d 139.0–151.2 (ddd $CF{=}CF_2$), and 129.4–136.3 ppm (ddd°$CF{=}CF_2$).

Anal. Calcd for $C_8H_6F_3NO$: C, 50.80%; H, 3.20%.
Found: C, 50.80%; H, 3.29%.

2.4. General procedure for the preparation of imide trimers

The dianhydride (1 mmol) was added to a stirred solution of the trifluorovinyl ether end-capping agent (2.2 mmol) in NMP (solids content 15 wt%) in a three-necked resin kettle equipped with a mechanical stirrer and a nitrogen inlet at room temperature. After the solution was stirred under nitrogen at room temperature for 12 h, pyridine (3 mmol) and acetic anhydride (3 mmol) were added. The resulting solution was stirred overnight at room temperature. The product was precipitated in stirred methanol, collected by filtration, washed with methanol, and dried under reduced pressure at 90°C for 6 h.

2.5. General procedure for the preparation of polyimides

The trimer (2.0 g) was melted in a disk-shaped glass mold 25 mm in diameter and 20 mm deep under reduced pressure. After complete melting, the mold was heated at 180°C for 2 h to remove any volatiles. The mold was back-filled with nitrogen and heated to 220°C for 12 h. The polymer was obtained as a light yellow solid.

3. Results and discussion

3.1. Synthesis of the end-capping agent 4-(trifluorovinyloxy)aniline (**3**)

The end-capping agent containing a trifluorovinyl ether moiety (**3**) was prepared by the route shown in Scheme 1. This route began with the conversion of 4-acetamidophenol to the phenoxide salt, which was dried, in situ, by azeotropic distillation. The salt was then treated with 1,2-dibromotetrafluoroethane (DBTE) in DMSO at 35°C to form **1**. The reaction of **1** with activated zinc granules in acetonitrile afforded compound **2**. The amine was deprotected with aqueous hydrochloric acid to afford TFVA (**3**), which was purified by column chromatography on basic alumina using a mixture of hexane and ethyl acetate as the eluent. The structure of compound **3** was ascertained by FTIR, ^{1}H-NMR, ^{13}C-NMR, and ^{19}FNMR. The presence of the trifluorovinyl functional group (–CF=CF$_2$) was substantiated by the absorption peak at 1833 cm^{-1} in the IR spectrum. It was also confirmed by the two doublets in three different regions (−121.9, −128.9, −134.0 ppm) in the ^{19}F-NMR spectrum [13].

The purification of **3** was difficult because it was hard to remove the major by-product 4-(1,1,2,2-tetrafluoroethoxy)-acetamidobenzene that was formed in the first two steps of the synthetic sequence. Proposed mechanisms for the formation of this by-product are shown in Scheme 2 [22]. The alkylfluorination is thought to follow an ionic chain mechanism. The phenoxide ion is slow to attack DBTE in the first step, but it reacts quickly with tetrafluoroethylene in the propagation step. The by-product is formed in the termination step. Thus, DBTE is both a brominating agent and a tetrafluorovinyl ether precursor. In the second step, 2-bromotetrafluoroethyl ether is treated with zinc to produce the trifluorovinyl ether functionality. The elimination reaction involves the abstraction of bromide followed by the loss of a fluoride ion. The conjugate base can also be attacked by a proton to form the by-product [15]. Thus, it is critical that the salt solution be absolutely dry. Treatment of the by-product with strong base or heating to high temperature does not eliminate hydrogen fluoride to form the trifluoroolefin, as elimination of phenol seems to be preferred under these conditions [23]. The separation of the by-product from the fluoroolefin is particularly troublesome because of the similarity of the two-fluorocarbon structures. The end-capping agent could not be used in the preparation of the trimers without removing the by-product, because the impurity would function as a chain-terminating agent that would limit the molecular weight during the subsequent step-growth cyclopolymerization. The only effective method for removing the by-product was column chromatography on basic alumina using a mixture of hexane and ethyl acetate as the eluent. This procedure took a long time, and the overall yield of pure **3** was only approximately 10%. The by-product could easily be detected with ^{1}H-NMR because of the characteristic three triplets at δ 5.5–6.3 ppm. The purity of the end-capping agent was confirmed by HPLC (acetonitrile/water: 6/4, UV detector, $\lambda = 254$ nm).

3.2. Preparation of imide trimers

Trifluorovinyl ether-terminated imide trimers were prepared by a two-step method as shown in Scheme 3. The end-capping agent containing the trifluorovinyl ether group was treated with two aromatic dianhydrides, i.e. BisA-DA and 6FDA, in NMP at room temperature to yield the corresponding amic acid precursors. These amic acids were converted to the trifluorovinyl ether-terminated imide trimers by chemical imidization with pyridine and acetic anhydride. The end-capped trimers were then isolated by precipitation in methanol or water. The structures of the trimers were ascertained by FTIR, ^{1}H-NMR, and ^{19}F-NMR. The FTIR spectra of the trimers contained absorptions at 1777, 1724, and 1361 cm^{-1}, characteristic of aromatic imide compounds [1]. The spectroscopic analysis clearly showed that no amic acid moieties were present in the products. The presence of the trifluorovinylether functionality was confirmed by FTIR and ^{19}F-NMR. The FTIR spectra contained an absorption at 1834 cm^{-1}, characteristic of the trifluorovinylether group [13]. The ^{19}F-NMR spectra contained two doublets in three different regions (−121.9, −128.9, −143.0 ppm) [13].

3.3. Thermal properties of the imide trimers

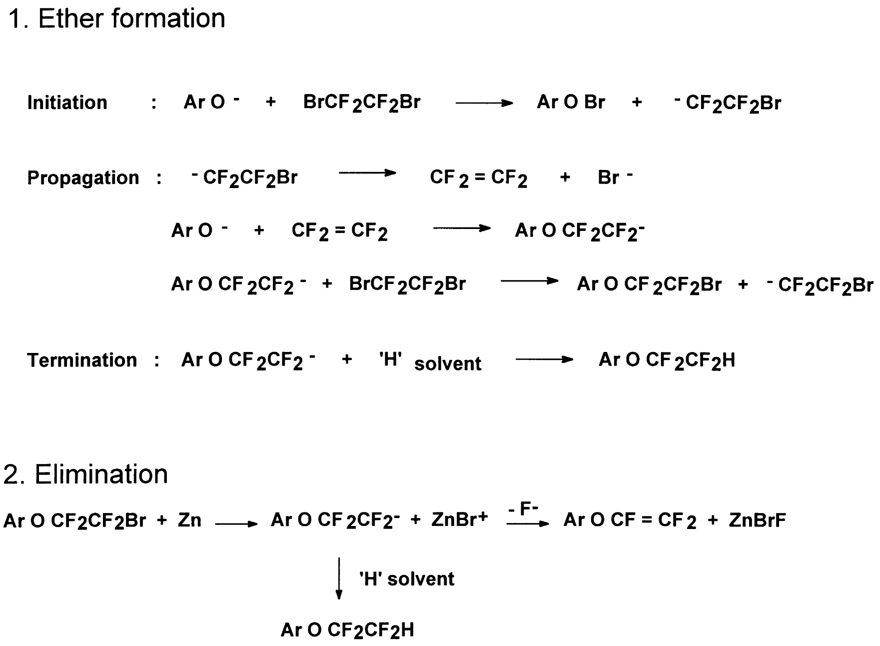
The imide trimers were subjected to DSC analysis in order to determine the difference between the trimer melting point and the temperature at which thermal dimerization of the terminal trifluorovinyl groups began. This difference, which is commonly referred to as the “processing window”, is an indication of the ease with which a reactive oligomer can be melt processed. The DSC thermogram of the imide trimer (**4**) prepared from BisA-DA and TFVA contained a melting endotherm with a minimum at 153°C and a thermal polymerization exotherm that began near 170°C with a maximum at 244°C (Fig. 1). Thus, the processing window was only about 17°C. The exothermic enthalpy of the reaction was about 35 kcal/mol. The analogous trimer prepared from 6FDA (**5**) melted lower near 136°C and then underwent an exothermic reaction starting near 175°C (Table 1). Hence, the processing window was considerably larger, i.e. approximately 39°C. The enthalpy of the exotherm was 35 kcal/mol, identical to that provided by **4**.

3.4. Polymerization of the imide trimers

The imide trimers were thermally polymerized as shown in Scheme 4. Thus, the trimer was placed in a mold and heated to the melting temperature under reduced pressure. After heating at 180°C for 2 h to remove any volatiles, the mold was flushed with nitrogen and heated at 220°C for 12 h to complete chain extension. The structures of the polyimide products (**6** and **7**) were confirmed by FTIR and ^{19}F-NMR analyses. The formation of the PFCB rings was ascertained by the appearance of the strong FTIR band at 961 cm^{-1}. In the ^{19}F-NMR spectra, the trifluorovinyl absorption bands completely disappeared and several new major fluorine peaks appeared that could be attributed to *cis* and *trans* substituted PFCB rings [13].

3.5. Polyimide properties

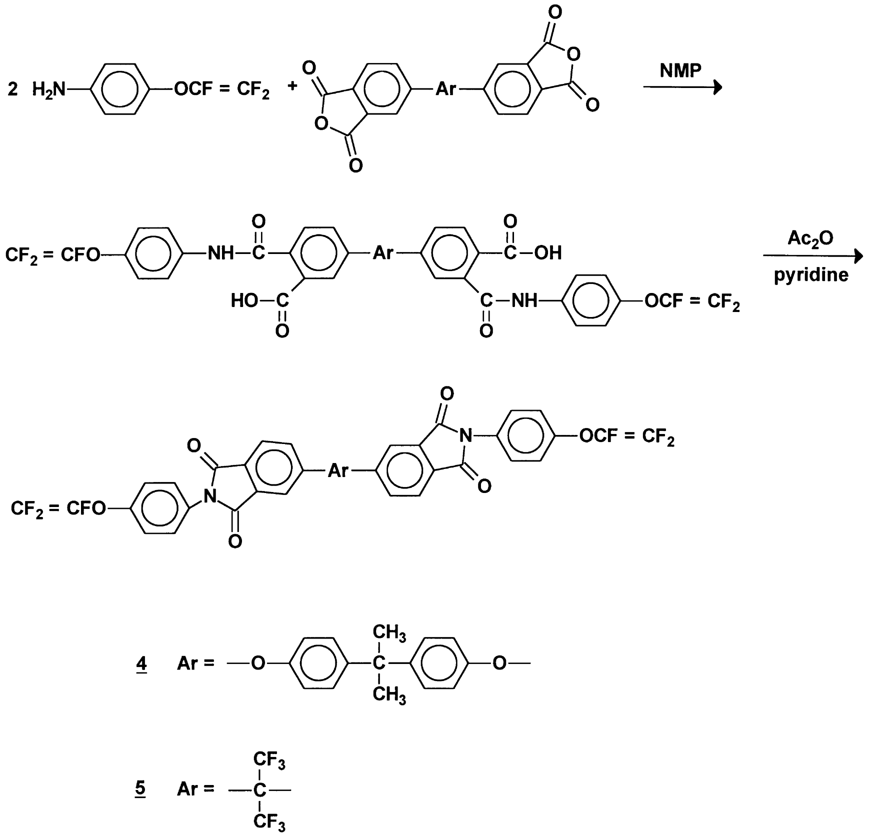
The BisA-DA-based polyimide **6** displayed limited solubility, while the 6FDA-based **7** was soluble in several common organic solvents (Table 2). The intrinsic viscosities of the polymers in NMP at 30.0 ± 0.1°C were 0.63 and



Scheme 2.

0.31 dl/g, respectively (Table 3). The number-average molecular weight ($\bar{M}$n) and weight average molecular weight ($\bar{M}$w) of **6** were determined to be 76,000 and 224,000, respectively, using GPC with polystyrene standards. However, it is speculated that these values are high. The thermal cyclodimerization of 4,4′-bis(trifluorovinyloxy)biphenyl previously gave a polyarylether with an ($\bar{M}$w) of 112,400 [16].

The T_gs of **6** and **7**, which were determined with DSC,



Scheme 3.

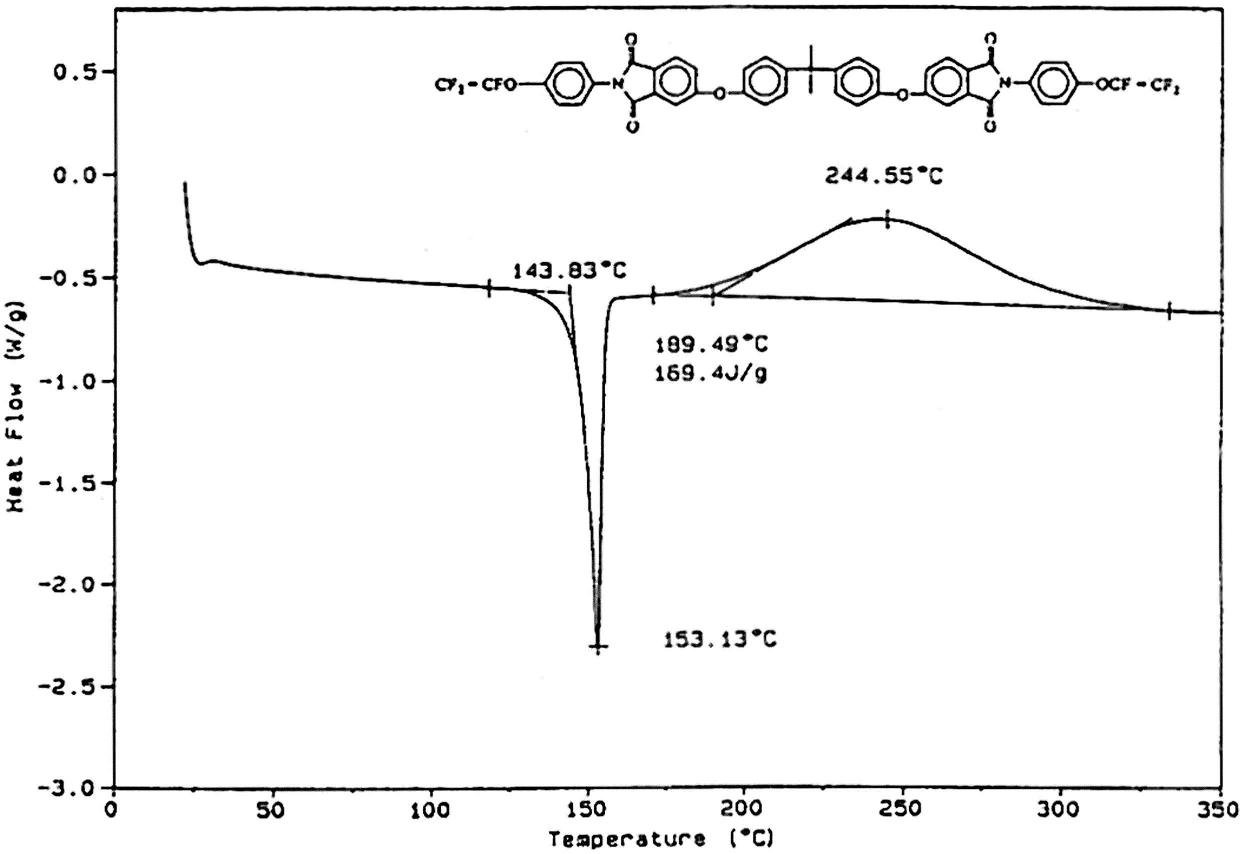


Fig. 1. DSC thermogram of TFVA-endcapped imide trimer **3**.

were 186 and 206°C, respectively (Table 3). The polymers displayed good thermo-oxidative and thermal stabilities. The BisA-DA-based **6** underwent 5% weight losses at 553°C in air and 563°C in nitrogen when subjected to TGA. The 6FDA-based **7** was slightly less stable undergoing 5% weight losses at 505°C in air and 519°C in nitrogen. The intrinsic viscosity measurements suggested that this polymer had lower molecular weight, which may have contributed to the reduced stability.

Polymer **6** was cast from NMP solutions into tough, flexible light brown films. The in-plane T_gs and CTEs of the thin films were determined with TMA utilizing a tension mode. Before the measurements were performed, each film was heated to slightly above the polymer T_g under 0.1 MPa tensile stress to release any internal stress that may have developed during film preparation and to provide a uniform thermal history. The films were then subjected to various stresses (1–6 MPa) and heated at a rate of 10°C/min. The T_g at each stress level was taken as the temperature at which a dramatic change in slope of the plot of film dimension versus temperature occurred. The in-plane T_g of the film showed a linear dependence upon the applied tensile stress. Increasing the tensile stress resulted in a lower T_g. This phenomenon has been attributed to increased free volume associated with stress [8]. A linear extrapolation of the T_g values to zero stress ($s = 0$) gave a T_g of 194°C (Fig. 2). This value is in good agreement with the T_g of 186°C determined by DSC analysis of a powder sample.

The CTE of the films was taken as the mean of the dimensional change between 50°C and 150°C at each applied stress. As the applied stress was increased, the CTE

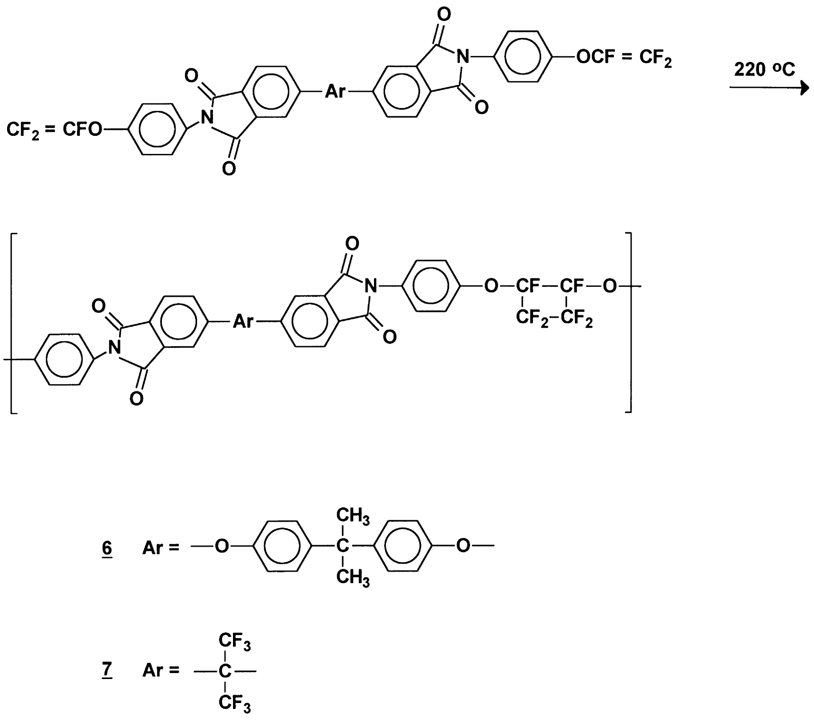
Table 1
Thermal properties of imide trimers endcapped with TFVA

Trimer	T_m[a] (°C)	T_{onset}[b] (°C)	T_{max}[c] (°C)	$-\Delta H_{pzn}$[d] (kcal/mol)
4	153	170	245	35
5	136	175	244	35

[a] Minimum in melting endotherm on DSC thermogram obtained with a heating rate of 10°C/min.
[b] Onset of polymerization exotherm on DSC thermogram.
[c] Maximum of polymerization exotherm.
[d] Determined from area under exothermic peak.

Table 2
Solubilities of polyimides containing PFCB (solubility: " − " denotes less than 2–3 g/l dissolved in solvent; " + " is for more than 2–3 g/l dissolved in solvent)

PIs	Acetone	THF	DMF	DMAc	NMP	$CHCl_3$
6	−	−	−	−	+	−
7	+	+	+	+	+	+



Scheme 4.

increased linearly in the stress range of 1–6 MPa. An extrapolation of the CTE values to zero stress gave a CTE of $57.1 \times 10^{-6}(°C)^{-1}$ (Fig. 2). Other fluorinated polyimides have been shown to display CTEs between 6 and $133 \times 10^{-6}(°C)^{-1}$ [8,9].

Dynamical mechanical analysis (DMA) of thin films of **6** was carried out at a frequency of 1 Hz. The behavior of the loss modulus (E') and the loss factor (tan δ) suggested that only one relaxation process was prevalent. The only relaxation (attributed to T_g) occurred at 194°C, which is an excellent agreement with the TMA results. There was no β relaxation observed even when the frequency was varied from 0.01 to 10 Hz.

The thin film mechanical properties and water absorption of **6** were determined by ASTM methods as shown in Table 4. The films exhibited a tensile strength of 88 MPa, a modulus of 2110 MPa, and an elongation at break of 5.9%. Thus, this polyimide displayed better mechanical properties than those of linear PFCB-containing poly(aryl ethers) [13]. This is most likely due to stronger intermolecular interactions in the polyimide. However, the PI water absorptions (0.08%) were slightly higher than those of the PFCB-containing poly(aryl ethers) (0.04%). This is probably due to the more polar imide linkages. The water absorption displayed by **6** is lower than that displayed by most fluorinated polyimides (0.1–3.8%) [9].

4. Summary and conclusions

The amine end-capping agent TFVA was synthesized from 4-acetamidophenol and DBTE. Imide trimers were

Table 3
Polyimide properties

Polyimide	$[\eta]$[a] (dl/g)	T_g[b] (°C)	TGA[c] (°C)	
			Air	N_2
6	0.63	186	553	563
7	0.31	206	505	519

[a] Determined in NMP at 30.0 ± 0.1°C.

[b] Mid point in the change in slope on the DSC thermogram obtained with a heating rate of 10°C/min.

[c] Temperature at which samples lost 5% of their weight when subjected to TGA with a heating rate of 20°C/min.

Table 4
Thin film properties of polyimide **6**

Tensile strength[a] (MPa)	Modulus[a] (MPa)	Elongation At Break[a] (%)	Water absorption[b] (%, 24 h)
88	2113	5.9	0.08

[a] Determined by ASTM D 882-91.

[b] Determined by ASTM D 570-81.

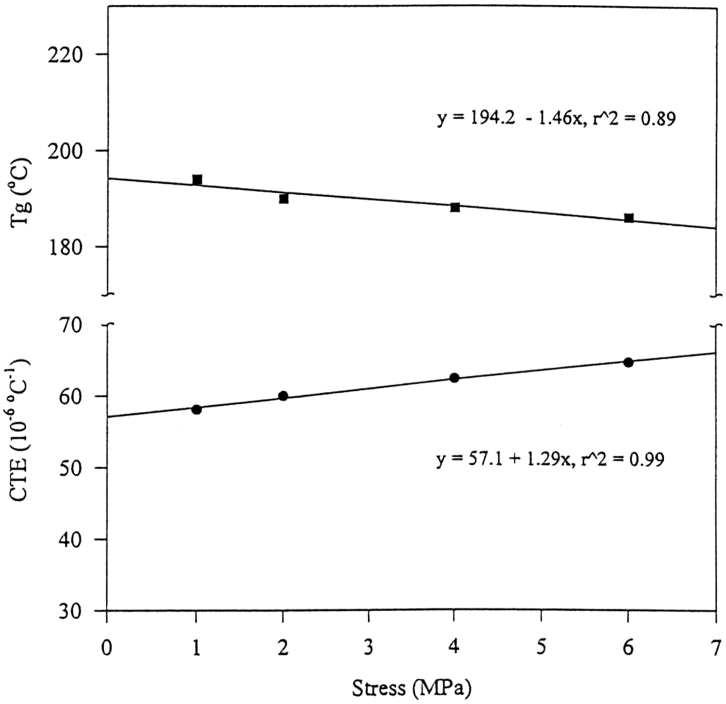


Fig. 2. Dependence of T_g and CTE on applied stress for PFCB-containing polyimide **6**.

prepared from the end-capping agent and BisA-DA and 6FDA. The trimer based on BisA-DA melted near 153°C and underwent thermal polymerization starting near 170°C. The trimer based on 6FDA melted near 136°C and underwent thermal polymerization starting near 175°C. The 39° processing window displayed by this trimer should allow it to be melt processed prior to chain extension. The PFCB-containing polyimides obtained had intrinsic viscosities of 0.63 and 0.31 dl/g and T_gs of 186 and 206°C, respectively. A thin film of the BisA-DA based polyimide displayed an in-plane CTE of $57.1 \times 10^{-6} (°C)^{-1}$, a tensile strength of 88 MPa, a modulus of 2110 MPa, an elongation at break of 5.9%, and a water absorption of 0.08%. Thus, the material appears to be suitable for high-performance composite and microelectronic applications.

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