Synthesis and Properties of Processable Polyimides Containing Diacetylene Groups

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Diacetylene-containing polyimides have been prepared by the oxidative coupling of new diethynyl diimide monomers. Condensation of various ethynyl-terminated amines with either 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) or pyromellitic dianhydride (PMDA) provided the monomers. Processability was enhanced by increasing the number of consecutive methylenes in the backbone, by incorporating aliphatic side chains, and for the 6FDA-based polyimides in general. The 6FDA-based diacetylene-containing polyimides are soluble in many common solvents including acetone. By controlling polymerization time, either oligomers or polyimides can be produced in high yield. High-resolution ^{1}H NMR and IR spectroscopy were used to monitor the polymerization. With the exception of the polyimides containing aliphatic side groups, thermal analysis reveals a diacetylene reaction exotherm that occurs without evolution of volatile byproducts; upon thermal annealing, the exotherm disappears and these polyimides become insoluble in all common solvents (i.e., cross-linked). Gas-transport properties are reported for one of the cross-linked 6FDA-based materials.

Introduction

Aromatic polyimides are well-known for high thermal stability and excellent solvent resistance,[1,2] properties that also hinder processability. Consequently, most polyimides are processed in the form of their soluble poly(amic acid) precursor. Compared to the fully imidized polymer, these poly(amic acids) are hydrolytically unstable[3] and can be corrosive.[4] After processing, thermal curing gives the polyimide. Water released by this cyclodehydration can result in microvoid formation,[5] with pronounced effects on polyimide properties. Use of polyimides in gas-separation membranes has been proposed based on their attractive transport properties. Yet, the formation of complex membrane structures has been difficult to achieve for all but a few highly soluble materials.

Processability of fully imidized polymers has been improved by altering repeat-unit structures in a variety of ways,[6] typically by introduction of more flexible linkages[7] or bulky groups.[8−11] This, however, has resulted in decreased glass transition temperatures and mechanical moduli. The seemingly incompatible combination of processability with excellent thermal stability and solvent resistance has been achieved through the development of cross-linkable polyimides[12−21] and imide oligomers.[22−32] Polyimides with flexible chain

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(1) Wilson, D., Stenzenberger, H. D., Hergenrother, P. M., Eds. *Polyimides*; Blackie and Son: Glasgow, 1990.

(2) Feger, C., Khojasten, M. M., McGrath, J. E., Eds. *Polyimides: Materials, Chemistry, and Characterization*; Elsevier: Amsterdam, 1989.

(3) Ghosh, M. K., Mittal, K. L., Eds. *Polyimides, Fundamentals and Applications*; Marcel Dekker: New York, 1996.

(4) Sroog, C. E. *Prog. Polym. Sci.* **1991**, *16*, 561.

(5) Bruma, M.; Schulz, B.; Mercer, F. W. *Polymer* **1994**, *35*, 4209.

(6) Huang, S. J.; Hoyt, A. E. *Trends Polym. Sci.* **1995**, *3*, 262.

(7) Boston, H. G.; Clair, A. K. S.; Pratt, J. R. *J. Appl. Polym. Sci.* **1992**, *46*, 243.

(8) Maier, G.; Yang, D.; Wolf, M.; Nuyken, O. *High Perform. Polym.* **1994**, *6*, 335.

(9) de la Campa, J. G.; Tauler, C.; Lozano, A. E.; de Abajo, J. *Macromol. Rapid Commun.* **1994**, *15*, 417.

(10) Yang, C.-P.; Lin, J.-H. *J. Polym. Sci.: Polym. Chem.* **1994**, *32*, 2653.

(11) Matsumoto, T.; Kurosaki, T. *Macromolecules* **1997**, *30*, 993.

(12) Moy, T. M.; Konas, M.; McGrath, J. E.; Fields, E. K. *J. Polym. Chem.: Polym. Chem.* **1994**, *32*, 2377.

(13) Sen, D.; Maiti, S. *Colloid Polym. Sci.* **1990**, *268*, 901.

(14) Takeichi, T.; Ogura, S.; Takayama, Y. *J. Polym. Sci.: Polym. Chem.* **1994**, *32*, 579.

(15) Takeichi, T.; Tanikawa, M. *J. Polym. Sci.: Polym. Chem.* **1996**, *34*, 2205.

(16) Gao, C.; Paventi, M.; Hay, A. S. *J. Polym. Chem.: Polym. Chem.* **1996**, *34*, 413.

(17) Chao, H. S.-I.; Vallance, M. A. *J. Polym. Sci.: Polym. Chem.* **1990**, *28*, 1209.

(18) Takeichi, T.; Date, H.; Takayama, Y. *J. Polym. Sci.: Polym. Chem.* **1990**, *28*, 1989.

(19) Jensen, B. J.; Hergenrother, P. M.; Nwokogu, G. *Polymer* **1993**, *34*, 630.

(20) Meyer, G. W.; Glass, T. E.; Grubbs, H. J.; McGrath, J. E. *J. Polym. Sci.: Polym. Chem.* **1995**, *33*, 2141.

(21) Southcott, M.; Amone, M.; Senger, J.; Wang, A.; Polio, A.; Sheppard, C. H. *High Perform. Polym.* **1994**, *6*, 1.

(22) Takeichi, T.; Stille, J. K. *Macromolecules* **1986**, *19*, 2103.

(23) Takeichi, T.; Stille, J. K. *Macromolecules* **1986**, *19*, 2093.

(24) Grenier-Loustalot, M. F.; Billon, L. *Polym. Int.* **1996**, *41*, 135.

(25) Tan, L.-S.; Arnold, F. E. *J. Polym. Sci.: Polym. Chem.* **1988**, *26*, 1819.

(26) Hergenrother, P. M. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1984**, *25*, 97.

(27) Moy, T. M.; DePorter, C. D.; McGrath, J. E. *Polymer* **1993**, *34*, 819.

(28) Takekoshi, T., Ed. *Polyimides*; Springer: Berlin, 1990.

(29) Capo, D. J.; Schoenberg, J. E. *SAMPE J.* **1987**, *23*, 35.

(30) Yamamoto, S.; Tanaka, H.; Fujii, K. U.S. Patent 5,081,196, 1992.

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structures and imide oligomers can be processed via melt or solution techniques and then cross-linked to provide imide-based materials with enhanced properties. While a variety of cross-linkable functionalities have been incorporated, the ethynyl group has been particularly popular. This group has been synthetically introduced at chain ends, internally, or in both locations. Thermal curing leads to cross-linked imide materials without the evolution of volatile byproducts. The resultant highly cross-linked structures can be brittle and thus liable to microcracking.

Ethynyl end-capped monomers and oligomers can be oxidatively coupled to produce diacetylene-containing polymers. Diacetylene-containing polyimides offer potential advantages as cross-linkable imide materials for membrane applications. For example, in properly designed systems, cross-linking may be activated both thermally and by radiation treatment, cross-linking-induced embrittlement may be avoided, and cross-linking-induced density changes may be minimized. The ability to cross-link by various treatments can be attributed to the versatility of diacetylenes as reactive groups. Besides 1,2- and 1,4-additions,[33] diacetylenes can act as both dienes and dienophiles in Diels−Alder-type cross-linking reactions.[34] The latter two potential advantages are related to the ability of diacetylenes to undergo a topochemically controlled solid-state 1,4-addition polymerization to give polydiacetylene cross-links.[35] Because specific packing geometries are needed for this reaction to occur, the cross-links can be restricted to the more ordered regions. Material ductility is maintained (and density increases are minimized) since the amorphous regions remain un-cross-linked.[36] A number of semicrystalline diacetylene-containing polymers have been selectively cross-linked in the crystalline regions by controlled exposure to electron beam radiation.[37] Above a characteristic threshold dosage, amorphous regions are also cross-linked through reactions other than the diacetylene to polydiacetylene conversion. The former cross-linking mode is referred to as "cross-polymerization",[38] while the latter mode is called "hypercrosslinking." Restriction of cross-links to more ordered regions may be particularly useful for applications such as membranes in which high transport rates are important (the denser, ordered regions contribute little to transport).[39]

Some diacetylene-containing polyimides have been prepared.[17,40−42] A class of diacetylene-terminated polyimides have also been reported for use as end-cross-linkable polyimide resin materials.[43] The diacetylene-containing polyimides based on pyromellitic dianhydride are largely unprocessable and used for moldings. Using these materials as a starting point, we have designed and synthesized new diacetylene-containing polyimides that can be processed into asymmetric membranes. To impart processability, flexibility was introduced into the backbone via longer sequences of consecutive methylenes, aliphatic side groups were incorporated, and the pyromellitimide unit was replaced with a 4,4′-(hexafluoroisopropylidene)bisphthalimide unit.[44] The synthesis, characterization, and thermal properties of these new polyimides are described below.

Experimental Section

All solvents and reagents were purchased from Aldrich and used without further purification. Fourier transform infrared spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 16 cm^{-1}. A total of 16 scans were averaged for solid samples prepared by the KBr pellet method. ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz. ^{13}C NMR spectra were recorded on a Bruker AMX 400 operating at 100 MHz.

The solubility of the diacetylene-functionalized polyimides was examined on 1 wt % solutions of the polymers in various solvents. Thermogravimetric (TG) and differential thermal analyses (DTA) were conducted on a Seiko TG/DTA 320 thermobalance operating at a heating rate of 10 °C/min in a nitrogen atmosphere. Unless stated otherwise, polymer samples were annealed in the thermobalance by heating at 10 °C/min to 300 °C and then cooled immediately; a second heating scan provided the TG/DTA thermogram for an annealed sample.

The general reaction scheme is shown in Figure 1. Polyimide structures are shown in the figure along with the acronyms used in this paper. Each monomer is named after the dianhydride from which it was produced, and the nature of the spacer group separating the diacetylene groups from the imide nitrogens. For example, the "1,1−6FDA" is a diimide monomer produced from 6FDA [4,4′-(hexafluoroisopropylidene)-diphthalic anhydride] that contains one methylene spacer on each side of the monomer separating the acetylene carbon from the imide nitrogen. "DM" means dimethyl, and "DE" means diethyl.

Monomer Synthesis. *N,N′-Dipropargylpyromellitimide (1,1-PMDA).* Propargylamine (5.5 g, 0.1 mol) was dissolved in 150 mL of *N*-methylpyrrolidinone (NMP) heated to 50 °C and treated portionwise with pyromellitic dianhydride (PMDA, 10.9 g, 0.05 mol). Stirring was maintained for 4 h under nitrogen at 50 °C, after which a mixture of 12 mL of acetic anhydride and 6 mL of pyridine was added. The brown reaction mixture was stirred for 6 h at 75 °C, allowed to cool to room temperature, filtered, and recrystallized (2×) from DMSO to give tan crystalline monomer. Yield 11.2 g (77%). MS (FAB) 292. IR (KBr, cm^{-1}) 3265, 694 (≡C−H); 2126 (C≡C); 1773, 1714 (C=O). ^{1}H NMR (DMSO-d_6, δ) 8.28 (s, aromatic), 4.42 (d, $^{4}J = 2.5$ Hz, CH$_2$), 3.30 (t, $^{4}J = 2.5$ Hz, ≡CH). Anal. Calcd for $C_{16}H_8N_2O_4$: C, 65.76; H, 2.76; N, 9.59; O, 21.89. Found: C, 65.62; H, 2.79; N, 9.57.

N,N′-Bis(1,1-dimethylpropargyl)pyromellitimide (1,1-DM−PMDA). Similar treatment of 9.2 g (0.1 mol) of 90% 1,1-dimethylpropargylamine and 10.9 g (0.05 mol) of PMDA, as described for 1,1-PMDA, yielded 12.4 g (71%) of monomer after recrystallization from MeOH/CHCl$_3$ (35:65). Mp (DTA) 230 °C. MS (FAB) 348. IR (KBr, cm^{-1}) 3255, 675 (≡C−H); 2112 (C≡C); 1770, 1720 (C=O). ^{1}H NMR (CDCl$_3$, δ) 8.19 (s, aromatic), 2.52 (s, ≡CH), 1.99 (s, CH$_3$). $^{1}\{H\}^{13}$C NMR (CDCl$_3$, δ) 165.8, 136.8, 118.0, 84.9, 71.7, 52.9, 29.1. Anal. Calcd for

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(31) Yamamoto, S.; Hirano, Y.; Fujii, K. U.S. Patent 5,241,018, 1993.

(32) *Reactive Oligomers*; Harris, F. W., Spinelli, H. J., Eds.; ACS Symposium Series 282; American Chemical Society: Washington, DC, 1985.

(33) Dawson, D. J.; Fleming, W. W.; Lyerla, J. R.; Economy, J. In *Reactive Oligomers*; Harris, F. W., Spinelli, H. J., Eds.; ACS Symposium Series 282; American Chemical Society: Washington, DC, 1985; pp 63−79.

(34) D'Alelio, G. F.; Waitkus, P. A. U.S. Patent 4,331,601, 1982.

(35) Wegner, G. *Makromol. Chem.* **1970**, *134*, 219.

(36) Beckham, H. W.; Rubner, M. F. *Polymer* **1991**, *32*, 1821.

(37) Beckham, H. W.; Spiess, H. W. *Macromol. Chem. Phys.* **1994**, *195*, 1471.

(38) Thakur, M.; Lando, J. B. *Macromolecules* **1983**, *16*, 143.

(39) Weinkauf, D. H.; Paul, D. R. *J. Polym. Sci.: Polym. Phys.* **1992**, *30*, 837.

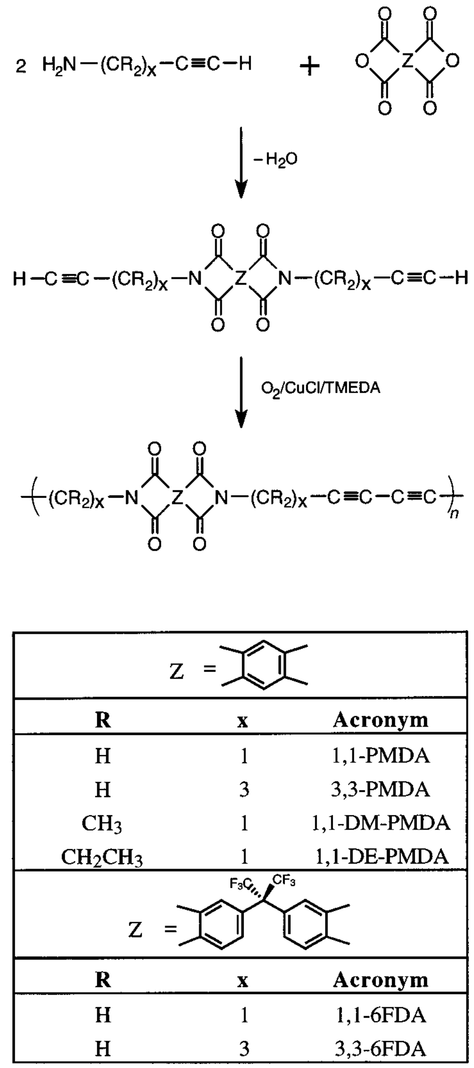
(40) Giesa, R.; Klapper, M.; Schulz, R. C. *Makromol. Chem., Makromol. Symp.* **1991**, *44*, 1.

(41) Tokushige, K.; Nakamura, K. Japan Patent 63-66227, 1988.

(42) Kato, J.; Tomino, N.; Imanishi, T.; Nakamura, K. *Kobunshi Ronbunshu* **1991**, *48*, 485.

(43) D'Alelio, G. F.; Waitkus, P. A. U.S. Patent 4,404,139, 1983.

(44) Scola, D. A.; Pater, R. H. U.S. Patent 4,569,988, 1986.



Z =

R	x	Acronym
H	1	1,1-PMDA
H	3	3,3-PMDA
CH_3	1	1,1-DM-PMDA
CH_2CH_3	1	1,1-DE-PMDA

Z =

R	x	Acronym
H	1	1,1-6FDA
H	3	3,3-6FDA

Figure 1. Two-stage general reaction scheme for the synthesis of diacetylene-containing polyimides. The first stage is a two-step ring-opening addition and cyclodehydration to give the α,ω-diethynyl dimide monomers. The second stage is the oxidative coupling polymerization. The table contains the acronyms used throughout this paper.

$C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04; O, 18.37. Found: C, 69.05; H, 4.67; N, 8.00.

N,N′-Bis(1,1-diethylpropargyl)pyromellitimide (1,1-DE−PMDA). Similar treatment of 5.7 g (0.05 mol) of 97% 1,1-diethylpropargylamine and 5.45 g (0.025 mol) of PMDA, as described for 1,1-PMDA, yielded 9.43 g (93%) white crystals after recrystallization from $CHCl_3$/MeOH (50:50). Mp (DTA) 159 °C. MS (FAB) 404. IR (KBr, cm^{-1}) 3278, 690 ($\equiv$C−H); 2126 (C$\equiv$C); 1764, 1720 (C=O). ^{1}H NMR ($CDCl_3$, δ) 8.19 (s, aromatic), 2.61 (s, $\equiv$CH), 2.55 (m, CH_2), 1.99 (m, CH_2), 1.01 (t, CH_3). $^1\{H\}^{13}C$ NMR ($CDCl_3$, δ) 166.1, 136.5, 117.9, 81.9, 74.5, 62.3, 32.0, 9.0. Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.26; H, 5.99; N, 6.93; O, 15.82. Found: C, 71.33; H, 6.02; N, 6.94.

5-Phthalimide-1-pentyne. In a 500-mL round-bottom flask containing 20.5 g (0.2 mol) of 5-chloro-1-pentyne, 37 g (0.2 mol) of potassium phthalimide and 200 mL of DMSO were added. The mixture was heated at 125 °C for 2 h with rapid stirring. The reaction mixture was allowed to cool, 400 mL of distilled water added, and the precipitate collected by filtration. Recrystallization from MeOH afforded 39.5 g (92%) of white crystals. Mp (Mel-temp) 88−90 °C. MS (FAB): 213. IR (KBr, cm^{-1}): 3267, 670 ($\equiv$C−H); 2126 (C$\equiv$C); 1768, 1707 (C=O). ^{1}H NMR ($CDCl_3$, δ) 7.84−7.69 (m, 4H, aromatic), 3.78 (t, NCH_2), 2.25 (dt, $CH_2C\equiv$), 1.94−1.89 (m, NCH_2CH_2), 1.90 (t, $\equiv$CH). $^1\{H\}^{13}C$ NMR ($CDCl_3$, δ) 168.3, 133.9, 132.2, 123.2, 83.0, 69.0, 37.2, 27.3, 16.3. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.59; O, 15.00. Found: C, 73.17; H, 5.23; N, 6.57.

5-Amino-1-pentyne. An ethanol (600 mL) solution of 5-phthalimide-1-pentyne (31.95 g, 0.15 mol) was stirred and heated to 70 °C in a 1-L 3-necked round-bottom flask fitted with a reflux condenser, a thermometer and a nitrogen inlet/outlet.[45] To this solution was added 10.5 mL (0.2 mol) of hydrazine monohydrate. The reaction mixture was maintained at 70 °C for 4 h, after which it was cooled to room temperature and 88 mL HCl (3 M) added. The resulting mixture was heated to 75 °C for 30 min, cooled, and filtered. The solid was washed with ethanol, and the ethanol layers were combined, concentrated, and filtered. The resulting solution was diluted with 200 mL of 2 N NaOH. This solution was extracted with 4 × 100-mL portions of CH_2Cl_2. The organic layer was dried with $MgSO_4$ and filtered. The filtrate was concentrated, and 8.78 g (70%) of a yellow oil was obtained. ^{1}H NMR ($CDCl_3$, δ) 2.67 (t, NCH_2), 2.12 (dt, $CH_2C\equiv$), 2.05 (s, NH_2), 1.84 (t, $\equiv$CH), 1.53 (m, NCH_2CH_2). $^1\{H\}^{13}C$ NMR ($CDCl_3$, δ) 83.7, 68.7, 40.7, 31.3, 15.8.

N,N′-Di-4-pentynylpyromellitimide (3,3-PMDA). Similar treatment of 5-amino-1-pentyne (4.15 g, 0.05 mol) and PMDA (5.45 g, 0.025 mol), as described for 1,1-PMDA, yielded 6.22 g (72%) of monomer after recrystallization (3×) from $CHCl_3$/MeOH (90:10). Mp (DTA) 195 °C. MS (FAB) 348. IR (KBr, cm^{-1}) 3278, 689 ($\equiv$C−H); 2112 (C$\equiv$C); 1763, 1714 (C=O). ^{1}H NMR ($CDCl_3$, δ) 8.26 (s, aromatic), 3.85 (t, NCH_2), 2.28 (dt, $CH_2C\equiv$), 1.95 (m, NCH_2CH_2), 1.89 (t, $\equiv$CH). $^1\{H\}^{13}C$ NMR ($CDCl_3$, δ) 166.2, 137.3, 118.2, 82.7, 69.2, 37.9, 27.0, 16.3. Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04; O, 18.37. Found: C, 68.84; H, 4.61; N, 8.00.

N,N′-Dipropargyl(4,4′-hexafluoroisopropylidene)bisphthalimide (1,1−6FDA). Propargylamine (5.5 g, 0.1 mol) dissolved in 100 mL of NMP at room temperature was treated portionwise with 22.2 g (0.05 mol) of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). A slow nitrogen flow was continuously employed throughout the reaction. The reaction was stirred at room temperature for 16 h, after which acetic anhydride (12 mL) and pyridine (6 mL) were added and the reaction temperature was raised to 75 °C for 6 h. After cooling, the solution was precipitated with a methanol/water mixture and filtered. The solid was recrystallized (3×) from MeOH to afford 24.4 g (94%) of crystalline monomer. Mp (DTA) 150 °C. MS (FAB): 518. IR (KBr, cm^{-1}) 3274, 678 ($\equiv$C−H); 2112 (C$\equiv$C); 1782, 1724 (C=O). ^{1}H NMR (acetone-d_6, δ) 8.1−7.9 (m, 6H, aromatic), 4.48 (d, ^4J = 2.5 Hz, CH_2), 2.80 (t, ^4J = 2.5 Hz, $\equiv$CH). $^1\{H\}^{13}C$ NMR (DMSO-d_6, δ) 165.8, 165.7, 137.4, 136.0, 132.7, 132.3, 124.2, 123.7, 123.3, 77.8, 74.0, 64.5, 27.0. Anal. Calcd for $C_{25}H_{12}F_6N_2O_4$: C, 57.93; H, 2.33; N, 5.40; F, 22.0; O, 12.36. Found: C, 58.03; H, 2.32; N, 5.34.

N,N′-Di-4-pentynyl(4,4′-hexafluoroisopropylidene)bisphthalimide (3,3−6FDA). Similar treatment of 5-amino-1-pentyne (4.15 g, 0.05 mol) and 11.1 g (0.025 mol) of 6FDA, as described for 1,1−6FDA, yielded 9.9 g (69%) of crystalline monomer after recrystallization (3×) from MeOH. Mp (DTA) 125 °C. MS (FAB) 574. IR (KBr, cm^{-1}) 3279, 690 ($\equiv$C−H); 2112 (C$\equiv$C); 1777, 1714 (C=O). ^{1}H NMR ($CDCl_3$, δ) 7.9−7.8 (m, 6H, aromatic), 3.80 (t, NCH_2), 2.26 (dt, $CH_2C\equiv$) 1.92 (m, NCH_2CH_2), 1.92 (t, $\equiv$CH). $\{^1H\}^{13}C$ NMR ($CDCl_3$, δ) 167.1, 166.9, 138.7, 135.5, 133.0, 132.7, 124.9, 123.6, 82.8, 69.2, 37.5, 27.2, 16.3 (CF_3 and CCF_3 not listed). Anal. Calcd for $C_{29}H_{20}N_2O_4F_6$: C, 60.63; H, 3.48; N, 4.88; F, 19.86; O, 11.15. Found: C, 60.98; H, 3.51; N, 4.98.

Polymer Synthesis. Polymers were obtained by the oxidative coupling of the difunctional terminal ethynylated monomers using a mixture of copper(I) chloride and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA).[46] The polymerization conditions for each polymer are summarized in Table 1. For each polymerization, the molar ratio of TMEDA:CuCl was 1.3:1. Solvents were chosen depending on which one solvated the

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[45] L'abbé, G.; Leurs, S.; Sannen, I.; Dehaen, W. *Tetrahedron* **1993**, *49*, 4439.

[46] Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275.

Table 1. Oxidative Coupling Polymerization of Ethynyl-Terminated Diimide Monomers

monomer	monomer amount (g)	solvent type/volume (mL)	CuCl amount (g)	reaction time (h)	temp (°C)
1,1-PMDA	2.92	DMSO/350	1.0	0.5	90
3,3-PMDA	1.74	DMSO/200	0.5	5	75
1,1-DM-PMDA	3.48	ODCB[a]/200	1.0	18	75
1,1-DE-PMDA	4.04	ODCB/100	1.0	18	75
1,1-6FDA	5.18	DMSO/60	0.75	18	25
3,3-6FDA	2.87	DMSO/60	0.5	18	25

[a] ODCB = *o*-dichlorobenzene.

polymer long enough for a reasonably high molecular weight to be achieved. The PMDA-based monomers were polymerized at high dilution and temperatures ≥ 75 °C; it is important to have both solvated PMDA and the CuCl/TMEDA mixture at these elevated temperatures prior to mixing to prevent precipitation. The polymerization mixture was cooled to 60 °C before precipitating the PMDA-based polymers. The 6FDA-based monomers were polymerized at room temperature since attempts at elevated temperatures produced only a dark insoluble mass.

All polymers were isolated as off-white to tan powders and kept screened from light during handling and storage (e.g., by wrapping glassware with Al foil). To ensure removal of copper, the polymers were redissolved and reprecipitated in acidified MeOH (when needed and when solubility was not a limitation). Soxhlet extraction with methanol was followed by drying at 60 °C under high vacuum for 48 h, except the 1,1-PMDA, which was dried at room temperature under high vacuum for 48 h. Removal of all residual solvent required much longer times or much higher temperatures, especially for the 6FDA-based materials. A typical polymerization was carried out by the following method:

Poly[N,N′-dipropargyl(4,4′-hexafluoroisopropylidene)bisphthalimide] (1,1−6FDA polyimide). A stirred solution of 1,1−6FDA monomer (5.18 g, 0.01 mol) in 40 mL of DMSO was mixed with a solution of CuCl (1.0 g, 0.01 mol) in 2.0 mL of TMEDA and 20 mL of DMSO. The reaction mixture was stirred under bubbling air for 18 h at room temperature and then poured into 200 mL of an acidified methanol/water mixture (4-mL of concentrated HCl in 96 mL of MeOH/300 mL of H_2O). The precipitate was filtered, washed several times with acidified methanol, Soxhlet-extracted with methanol for 48 h, and dried under high vacuum at 60 °C for 48 h.

Results and Discussion

Synthesis and Characterization. The diacetylene-containing polyimides were prepared in two stages via the general reaction scheme shown in Figure 1. The first stage is the preparation of the diimide monomers by a two-step method that entails (1) the ring-opening addition of a tetracarboxylic acid dianhydride to a solution containing 2 equiv of an ethynylated amine and (2) subsequent cyclodehydration of the generated amic acids by adding acetic anhydride and pyridine (2:1 ratio) to the amic acid solutions at elevated temperatures. The creation of the imide heterocycle in these monomers was monitored by FTIR. Cyclization was deemed complete once characteristic bands of the amic acid were replaced by those characteristic of the imide group: 1780 and 1720 cm^{-1} for the carbonyl band and 1380 cm^{-1} for the C−N absorption. The yields are quite high and the monomers highly crystalline. Multiple recrystallizations produced high-purity monomers as evidenced by ^1H NMR, ^{13}C NMR, mass spectroscopy, and elemental analysis.

Synthesis of the polymers is relatively straightforward via oxidative coupling[46] of the monomers containing preformed imide rings and terminal ethynyl groups. The diacetylene groups are created during the polymerization. Since the imide ring is already contained in the monomer, the disadvantages associated with post-processing curing of poly(amic acids) are avoided.

The IR spectra of the monomers exhibit strong absorption bands at 3300 and 670 cm^{-1} that correspond to the stretching and bending frequencies, respectively, of the bond connecting the terminal hydrogen to the sp-hybridized carbon of the ethynyl group. The disappearance of these bands in the IR spectra recorded after the oxidative polymerization is indicative of polymer formation with reasonable molecular weight. The prominent absorption at around 3300 cm^{-1} is completely absent for the polymers reported here.

^1H NMR spectroscopy was used for structure determination of monomers and polymers. The resonance observed for the end-group ethynyl proton (≡CH) in the monomer disappears in the polymer following the oxidative coupling. No residual signal due to unreacted terminal ethynyl groups was observed for any of the soluble polyimides. By limiting the polymerization time, ethynyl-terminated diacetylene-containing imide oligomers can be formed. Residual ethynyl protons in the ^1H NMR spectra can be integrated to determine the number-average degree of oligomerization. Ethynyl-terminated pentamers of 1,1−6FDA have been synthesized and characterized.[47] These ethynyl-terminated oligomers were not good film formers but were quite useful as cross-linkable additives in blends with structurally similar polyimides based on 6FDA. The low molecular weight of the 1,1−6FDA used in these blends was beneficial in this case for enhanced miscibility.[48]

The ^{13}C NMR spectra of the monomers and the polymers were obtained to ensure that the terminal ethynyl carbons were indeed transformed during the polymerization to diacetylenic carbons. The ^{13}C NMR spectra of 1,1-DM−PMDA and the polyimide produced from this monomer are shown in Figure 2. The peak assignments in the spectra were facilitated by a combination of DEPT (distortionless enhancement by polarization transfer) and undecoupled ^{13}C NMR spectroscopy. The only significant differences in the spectra are the disappearance of the two terminal ethynyl carbons at 85 and 72 ppm and the appearance of two new diacetylene carbons at 80 and 68 ppm. All of the other peaks appear at the same chemical shifts for the monomer and polymer. These observations were the same for all the soluble diacetylene-containing polyimides.

Solubility. The solubilities of the diacetylene-functionalized polyimides in various solvents are sum-

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(47) Karangu, N. T.; Rezac, M. E.; Beckham, H. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater.)* **1997**, *76*, 316.

(48) Rezac, M. E.; Sorenson, E. T.; Beckham, H. W. *J. Membr. Sci.* **1997**, *136*, 249.

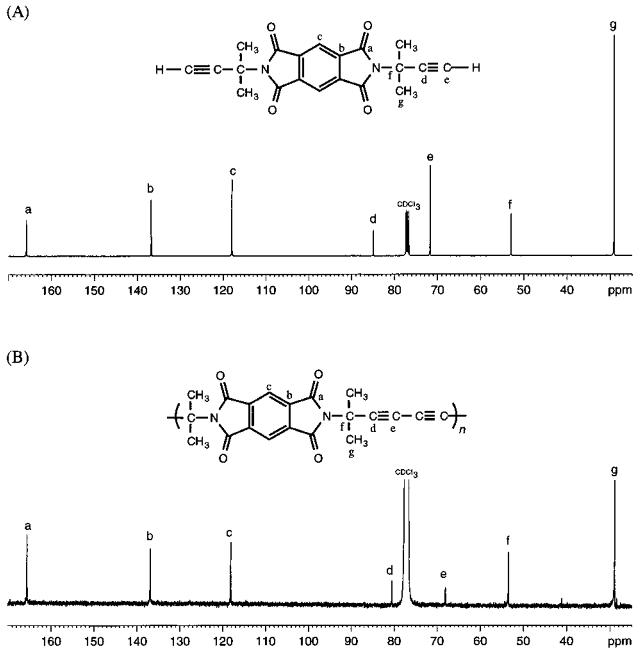

Figure 2. ^{13}C NMR spectra of (A) 1,1-DM-PMDA and (B) the polyimide produced by the oxidative coupling of this monomer. The ethynyl carbons at 85 and 72 ppm become diacetylenic carbons (80 and 68 ppm) after the polymerization.

marized in Table 2. As reported previously, the polyimide of 1,1-PMDA is essentially intractable. It is only partially soluble in hot *m*-cresol. Increasing the number of consecutive methylenes in the backbone improved the solubility: The polyimide of 3,3-PMDA was soluble in *m*-cresol, hot DMAc, and hot NMP. The 1,1-DM−PMDA and 1,1-DE−PMDA polyimides are soluble in a variety of hot solvents, indicating that aliphatic side chains also improved solubility. The most dramatic improvement in solubility was observed for the polyimides of 1,1−6FDA and 3,3−6FDA. By replacing the PMDA moiety with the 6FDA unit, the resulting polyimides are soluble in a variety of solvents at room temperature. The improved solubility of the 6FDA-based polymers compared to the PMDA-based polymers has been observed previously.[49] It can be explained by the disruptive nature of the hexafluoroisopropylidene units, which interfere with chain packing and consequently facilitate solvation. It is interesting to note that the 3,3−6FDA polyimide is soluble in chloroform at room temperature, while the 1,1−6FDA polyimide is not. Thus, solubilities for both PMDA-based and 6FDA-based polyimides are improved by increasing the number of consecutive methylenes along the backbone.

Coherent, transparent films were formed of the 1,1−6FDA and 3,3−6FDA polyimides by casting from acetone solutions. The 3,3−6FDA polyimide appears to be the best film-former. These were the only two polyimides for which molecular weights were estimated by gel permeation chromatography. Inherent viscosities were also determined. The results from both determinations are shown in Table 3.

Thermal Properties. The diacetylene-containing polyimides were analyzed by simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) under a nitrogen atmosphere. Thermal properties extracted from these data are summarized in Table 4. On the basis of thermal analyses alone, the six polyimides may be divided into two groups: (1) those with aliphatic side groups α to the diacetylenes and (2) those without. The TG/DTA scans for the 1,1-DE−PMDA polyimide is similar to the TG/DTA scan for the 1,1-DM−PMDA polyimide. Compared to the other four polyimides, these side-group-containing polyimides exhibit weight loss at lower temperatures, and no exotherm until after degradation (marked by significant weight loss).

The four polyimides with no aliphatic side groups exhibit moderate thermal stability (for polyimides), with no significant weight loss below 350 °C. Figure 3 shows the TG/DTA scans for the 3,3−6FDA polyimide. The exotherm is attributed to cross-linking via reactions of the diacetylene groups in the polymer backbone. It occurs at temperatures well before any significant degradative weight loss, an indication that curing proceeds without evolution of volatiles. This is true also for the polyimides of 1,1-PMDA, 3,3-PMDA, and 1,1−6FDA. The 10% weight-loss temperatures for these four polyimides are similar (410−430 °C), with the 3,3−6FDA polyimide exhibiting slightly superior thermal properties (see Table 4).

In general, the char yield decreased with increasing aliphatic character of the polyimide structure. The 1,1-PMDA and 1,1−6FDA polyimides have higher char yields (48 and 50%, respectively) than all the other polymers and possess single CH_2 groups between the imide nitrogens and the diacetylene carbons. The polyimides of 1,1-DM−PMDA, 3,3-PMDA, and 3,3−6FDA each have C_3H_6 structures between the imide nitrogens and diacetylene carbons. These polyimides registered char yields of 33, 38, and 35%, respectively. The 1,1-DE−PMDA polyimide had a char yield of 18%, which reflects the presence of the larger aliphatic group (C_5H_{10}).

Cross-Linking. All of the polyimides based on the linear propargylamines (1,1-PMDA, 3,3-PMDA, 1,1−6FDA, and 3,3−6FDA) exhibit exothermic peaks ranging from 217 to 288 °C in their DTA curves. Since these exotherms occur without weight loss, thermally activated cross-linking is suggested. They all become rust red upon annealing at elevated temperatures. Upon exposure to UV radiation (254 nm), the 1,1-PMDA and 3,3-PMDA polyimides become deep orange, the 3,3−6FDA polyimide becomes yellow, and the 1,1−6FDA polyimide exhibits no color change (this is true only for the completely dried materials). Color changes in diacetylene-containing polymers have long been associated with cross-linking via diacetylene cross-polymerization to give a conjugated polydiacetylene backbone.[35] On the basis of these observations alone, the PMDA-based materials are more easily cross-linked than the 6FDA-based materials. In fact, the 1,1-PMDA polyimide very quickly changes color simply upon exposure to sunlight. This may simply reflect the higher degree of order, necessary for diacetylene cross-polymerization, achievable in PMDA-based versus 6FDA-based polyimides.

TG and DTA thermograms of the annealed 3,3−6FDA polyimide are shown in Figure 3 along with those of the

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(49) St. Clair, A. K.; St. Clair, T. L.; Shevket, K. I. *Polym. Prepr. (Am. Chem Soc., Div. Mater. Sci. Eng.)* **1984**, *51*, 62.

Table 2. Solubilities of Diacetylene-Functionalized Polyimides

polymer		solvent						
		DMSO	NMP	DMAc	*m*-cresol	$CHCl_3$	acetone	THF
1,1-PMDA	cold	− −	− −	− −	− −	− −	− −	− −
	hot	− −	− −	− −	− +			
3,3-PMDA	cold	− −	− −	− −	+ +	− −	− −	− −
	hot	− +	+ +	− +				
1,1-DM−PMDA	cold	− −	− −	− −	− +	− +	− −	− −
	hot	− +	+ +	− +	+ +			
1,1-DE−PMDA	cold	− −	− −	− −	− +	+ +	− −	− −
	hot	− +	+ +	− +	+ +			
1,1-6FDA	cold	+ +	+ +	+ +	+ +	− −	+ +	+ +
	hot							
3,3-6FDA	cold	+ +	+ +	+ +	+ +	+ +	+ +	+ +
	hot							

[a] Solubility: + + completely soluble, − + partially soluble (i.e., cloudy solution), − − insoluble. Hot treatment was not conducted for chloroform, acetone, or THF.

Table 3. Molecular Weights of 6FDA-Based Materials

polymer	viscometry[a] η_{inh}	gel permeation chromatography[b]		
		M_n (g/mol)	M_w (g/mol)	M_w/M_n
1,1-6FDA	0.36	16,000	31,000	1.9
3,3-6FDA	0.42	9,000	44,000	4.9

[a] NMP, 30 °C, 0.5 g/dL. [b] THF (0.7 mL/min), refractive index detector, polystyrene standards.

Table 4. Thermal Properties of Diacetylene-Functionalized Polyimides

polymer	reaction exotherm (°C)	1% wt loss (°C)	10% wt loss (°C)	char yield at 500 °C (%)
1,1-PMDA	217	345	410	48
3,3-PMDA	288	340	420	38
1,1-DM-PMDA		185	315	33
1,1-DE-PMDA		190	310	18
1,1-6FDA[a]	257	330	410	50
3,3-6FDA[b]	244	390	430	35

[a] TG data are for sample annealed in thermobalance. [b] Dried further in thermobalance at 150 °C for 15 min.

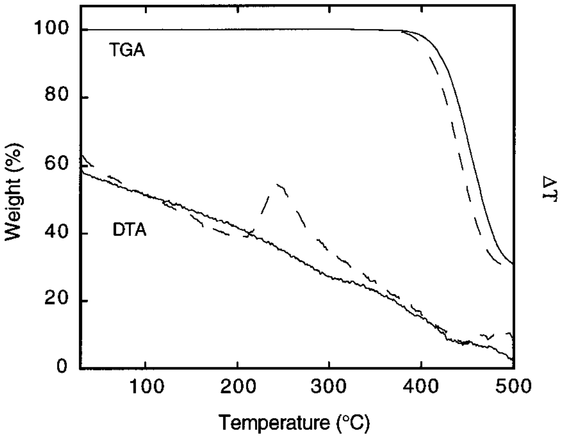

Figure 3. TGA and DTA curves of the 3,3−6FDA polyimide (—), and the same material after annealing (− − −). Prior to analysis, this polymer was dried in the thermobalance for 15 min at 150 °C to remove residual solvent. Annealing was conducted in the thermobalance by heating at 10 °C/min to 300 °C and then cooling immediately. Measured in nitrogen at 10 °C/min.

unannealed 3,3−6FDA polyimide. The exothermic peak at 244 °C disappears after thermal annealing, and the temperature-induced weight loss is not significantly affected. The solvent resistance, however, is greatly improved. As opposed to the 1,1-PMDA polyimide, the 3,3−6FDA polyimide is very soluble in a number of common organic solvents (see Table 2). After thermal annealing, it is insoluble in all solvents listed in Table 2. These results were observed for all of the polyimides based on the linear propargylamines: Following annealing, the thermal stability is maintained and the solvent resistance is greatly improved.

The two polyimides with side groups α to the diacetylene carbons (1,1-DM−PMDA and 1,1-DE−PMDA) do not exhibit exothermic peaks until degradative weight loss begins. It is postulated that the side groups sterically interfere with diacetylene cross-linking. It is known that diacetylene cross-polymerization occurs only when carbons 1 and 4 of adjacent diacetylene groups are within 0.4 nm of each other.[50] For the 1,1-DM−PMDA and 1,1-DE−PMDA polyimides, the side groups certainly preclude this type of cross-linking, and possibly other types as well if they depend on close approach of the diacetylene groups.

The molecular structures resulting from the thermally induced reactions giving rise to the exotherm in Figure 3 are unknown. At least three general classes of reactions can occur: (1) diacetylene cross-polymerization, (2) diacetylene hypercross-linking, and (3) ethynyl end-group reactions. Much work has already appeared concerning the products of the first and third processes,[51−55] but very little is known about diacetylene hyper-cross-linking. We are currently investigating the thermally activated cross-linking of these diacetylene-containing polyimides with a combination of solid-state NMR, IR, and Raman spectroscopies.

Permeability. Ultimately, we are interested in the possibility of using these materials for membranes to separate gases at elevated temperatures or in chemically aggressive environments. Thus, those materials which are thermally stable, cross-linkable, and can be processed from common solvents are of greatest interest. The transport properties of the 1,1−6FDA and the 3,3−6FDA material are currently under investigation. Pre-

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(50) Enkelmann, V. *Adv. Polym. Sci.* **1984**, *63*, 91.

(51) Grenier-Loustalot, M. F.; Sanglar, C. *High Perform. Polym.* **1996**, *8*, 315.

(52) Huang, W. X.; Wunder, S. L. *J. Appl. Polym. Sci.* **1996**, *59*, 511.

(53) Swanson, S. A.; Fleming, W. W.; Hofer, D. C. *Macromolecules* **1992**, *25*, 582.

(54) Lind, A. C.; Sandreczki, T. C.; Levy, R. L. Characterization of Acetylene-Terminated Resin Cure States, McDonnell Douglas Research Laboratories, 1984.

(55) Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Schaefer, J. *Macromolecules* **1979**, *12*, 423.

Table 5. Gas Transport Properties[a]

Polymer	permeability (barrer)[b] He	N_2	O_2	CO_2	CH_4	ideal selectivity He/CH_4	O_2/N_2	CO_2/N_2
1,1-6FDA cross-linked	41.9	0.19	1.3	3.9	0.18	230	6.9	20.6
6FDA-IPDA[c,d]	71.2	1.34	7.5	30.0	0.70	100	5.6	22.4
polysulfone[d]	10.8	0.18	1.2	4.6	0.18	60	6.0	25.6

[a] 10 atm, 35 °C. [b] 1 barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cm (Hg). [c] IPDA = 4,4′-isopropylidenedianiline. [d] Koros, W. J.; Fleming, G. K.; Jordon, S. M.; Kim, T. H.; Hoehn, H. H. *Prog. Polym. Sci.* **1988**, *13*, 339.

liminary results for a cross-linked (annealed at 205 °C for 8 h) sample of the 1,1−6FDA polymer are presented in Table 5.[56] Also presented are data for polysulfone, one of the most common materials for gas separation membranes, and a polyimide with a similar structure (6FDA−IPDA) but which is not cross-linkable and therefore not chemically resistant in the final state. The permeabilities reported were measured at 10 atm differential pressure and 35 °C using a standard constant-volume/variable-pressure apparatus.[57]

Analysis of the data presented in Table 5 indicates that the cross-linked 1,1−6FDA polymer possesses an attractive combination of permeability and selectivity. The permeation rates for helium in the cross-linked 1,1−6FDA is approximately 4 times that of the standard polysulfone. Furthermore, the ability to separate helium from the slower gases is markedly improved (He/CH_4 values of 230 compared to 60). When the two polyimides are compared, the permeation and permselectivity values are not radically different. Thus, even though the current material has been annealed to impart chemical resistance via cross-linking, the ability to transport gases is comparable to that of a highly soluble polyimide.

Conclusions

New diacetylene-containing polyimides have been synthesized in a relatively simple two-stage process from propargylamines and either PMDA or 6FDA. The 6FDA-based polyimides are soluble in a number of common organic solvents including acetone. When the amine is linear, thermally induced cross-linking occurs without evolution of volatiles. The soluble 3,3−6FDA polyimide may also be cross-linked by exposure to UV radiation. The cross-linked polyimides are insoluble in common solvents and their thermal stabilities uncompromised compared to their un-cross-linked analogues. These imide materials may be processed into films and membranes and then cross-linked in the solid state to enhance solvent resistance and temperature stability.

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(56) Bayer, B. Diplomarbeit, Institut für Thermische Verfahrenstechnik der Universität Karlsruhe (TH), 1996.

(57) O'Brien, K. C.; Koros, W. J.; Barbari, T. A.; Sanders, E. S. *J. Membr. Sci.* **1986**, *29*, 229.