Donor-Embedded Nonlinear Optical Side Chain Polyimides Containing No Flexible Tether: Materials of Exceptional Thermal Stability for Electrooptic Applications

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ABSTRACT: We describe here the preparation and characterization of the first processible nonlinear optical (NLO) polyimide where the chromophore is not incorporated using a flexible tether functionality. The polymer has a very high glass temperature and shows exceptional thermal and chemical stability. Poled samples also show outstanding orientational stability, consistent in part with the high glass transition temperature.

Introduction

Current wisdom dictates that fully integrated electrooptic switches and modulators will operate continuously at elevated temperatures (80−100 °C) and may experience brief excursions to 250 °C or more during the integration and packaging process.[1,2] This places additional demands on poled polymeric materials beyond simple bulk nonlinearity[3] and means that practical materials will need to display exceptional thermal stability of both polymer and chromophore as well as the induced polar order. While the latter has been greatly improved by various cross-linking schemes,[4] this technique often leads to processing problems in the formation of polymeric waveguiding devices.

Recently, attention has been focused on processible NLO thermoplastic polymers with high glass transition temperatures.[4] This has led to the study of functionalized polyimides, materials with excellent thermal stabilities and good optical characteristics.[5] These studies have included both host−guest composites[6−11] and chemically bound side chain polyimides.[12−19] While significant advances have been made recently in the latter class, most of the incorporated NLO chromophores have contained dialkylamino donor substituents and all have been attached via flexible alkyl or alkoxyalkyl tether groups, either incorporated into the main chain or contained in the side chain. We have demonstrated previously that dialkylamino donor substitution is a serious source of chromophore instability at high temperatures.[20] Furthermore, while flexible alkyl and hydroxyalkyl tether groups facilitate electric field poling, they tend to lower the T_g of the polymer, adversely affecting orientational stability. In addition, they can be a source of thermal instability at high temperatures.

We now report the synthesis of an NLO functionalized aromatic diamine monomer containing no flexible tether group which can be directly incorporated into polyimides by standard condensation polymerization techniques. The result is a soluble, rigid, functionalized donor-embedded side chain polyimide with a very high T_g (at least 100 °C greater than that for any reported chemically incorporated NLO polyimide), exceptional thermal stability, approaching that of ordinary polyimide dielectrics, and a polar order stability which is truly remarkable for a thermoplastic material.

Results and Discussion

For our initial studies, we have chosen the NLO functionalized aromatic diamine M1. This material could not be prepared by classical diazo coupling techniques because of the tendency of triarylamine derivatives substituted with strongly electron-donating substituents (RO, R_2N, RCONH, CF_3CONH, etc.) to undergo dearylation reactions.[21,22] The desired diamine M1 could, however, be prepared simply by controlling the stoichiometry of the Mills condensation as shown in Scheme 1. The diamine M1 is highly crystalline and can be recrystallized to high purity.

The monomer was incorporated into a variety of polyimides via condensation polymerization as shown in Scheme 2. The particular example in this scheme, employing (hexafluoroisopropylidene)diphthalic anhydride (6FDPA (**7**)) as a starting material, is chosen for illustration, since the fully imidized material (PI-1) is soluble in a number of common organic casting solvents. The glass temperature of PI-1, as determined by either differential scanning calorimetry (DSC) or dynamic mechanical thermal analysis (DMTA), was very high (T_g ~ 350 °C), reflecting the increased rigidity of the donor-embedded structure.

The thermal and chemical stability of PI-1 is exceptional as revealed both by thermal analysis (Figure 1a,b) and by variable-temperature UV−visible studies (Figure 2). Figure 1a shows that the value for T_5 (5% weight loss) occurs above 500°C, while the onset decomposition temperature (T_d)[20] is greater than 400 °C. Both values are significantly higher than those observed for side chain polyimides with either dialkyl- or diarylamino donor substitution and flexible alkyl tethers. Figure 1b shows the DSC curves of PI-1 in comparison with two other side chain polyimides (PI-2 and PI-3). PI-3 provides an example of diarylamino donor substitution in the chromophore,[21] a feature which has been demonstrated to significantly improve the thermal stability in many cases.[20]

Perhaps the most reliable criterion for thermal and chemical stability of a NLO functionalized polymer is provided by variable-temperature UV−visible studies. Figure 2 shows the effect of heating on the long-

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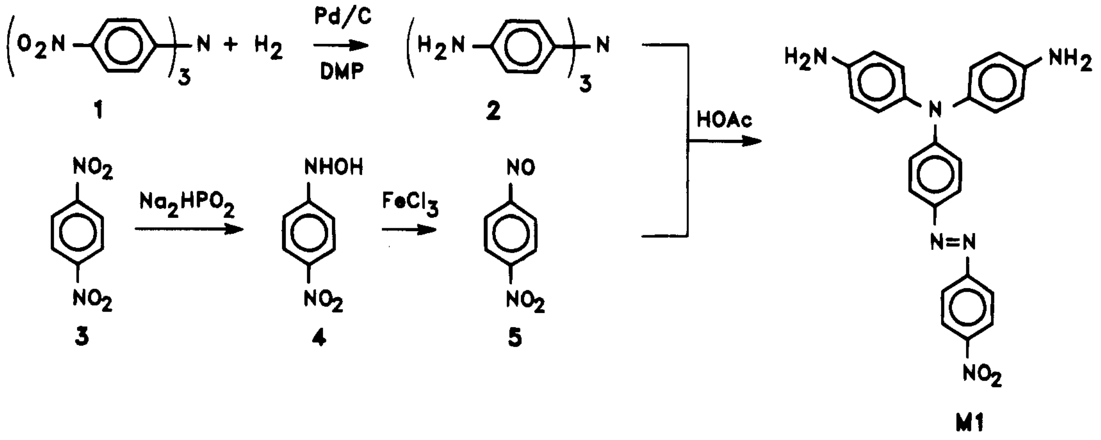
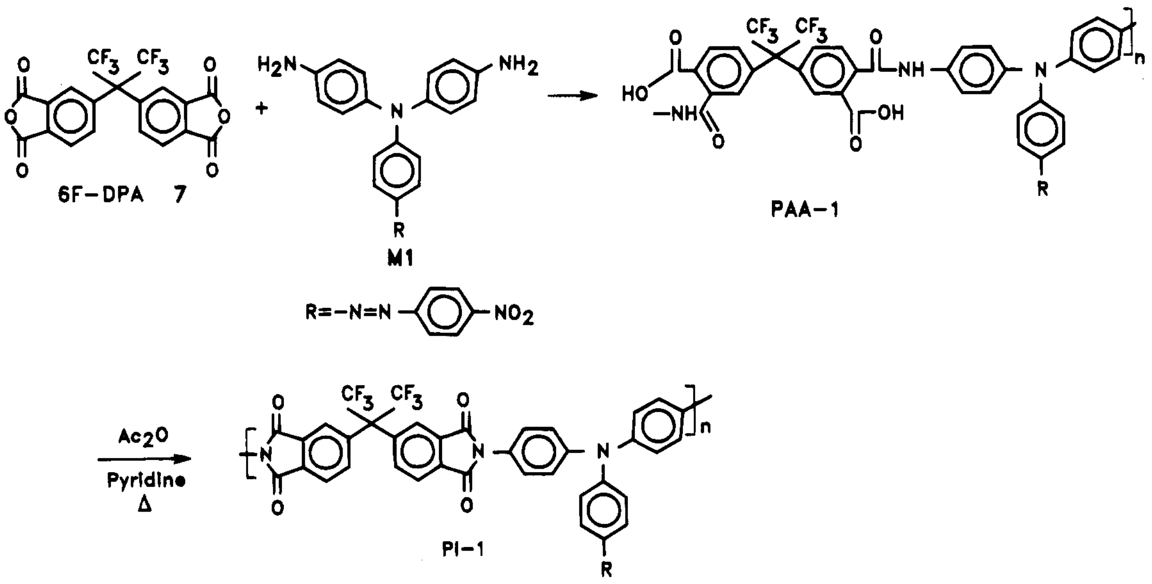
Scheme 1. Preparation of the NLO Substituted Aromatic Diamine Monomer M1



Scheme 2. Preparation of the NLO Polyimide PI-1 by Condensation Polymerization



wavelength visible transitions of PI-1, PI-2, and PI-3 (Chart 1). The reproducibility of the absorbance measurements with accurate sample positioning is ±3%. While PI-1 is stable for long periods at 350 °C, the absorptions of the other examples degrade at much lower temperatures. The donor-embedded material (PI-1) is even reasonably stable for brief periods (~20 min) at temperatures up to 375 °C (less than 20% absorbance loss).

High-quality films could be cast from either the poly(amic acid) solutions (PAA-1, NMP–15% xylenes) or the polyimide itself (PI-1, cyclopentanone). The poly(amic acid) films were poled in a corona field while simultaneously curing at 1 °C/min from 140 to 250 (280) °C. The preimidized material (PI-1) could be poled at 310 °C using either corona or electrode poling techniques.[4] The bulk nonlinearity of the corona-poled samples, as estimated by the intensity of the second harmonic signal (1.047 μm fundamental), was qualitatively similar for both the PAA-1 and PI-1 samples. The r_{33} coefficient for a sample of PI-1 (electrode poling 75 V/μm) was determined by ellipsometry[23,24] to be ~1.7 pm/V at 1.3 μm. In these preliminary experiments, relatively low poling fields were applied to a single-layer structure (1.2–1.6 μm) to ensure that the film integrity was maintained during poling, and the poling conditions are clearly unoptimized at this point. Extrapolation of the poling field to the higher values of 250–300 V/μm, which are routinely achieved in a three-layer stacked modulator configuration (two buffer layers sandwiching the NLO layer),[22] would predict a respectable r_{33} value of 6–7 pm/V at 1.3 μm. Calculations[25] for this polymer based on the chromophore molecular hyperpolarizability and loading level would suggest a maximum electrooptic coefficient at 1.3 nm of 9.5–10.5 pm/V at 310 °C and a poling field of 250 V/μm. The importance of the buffer layers in a stacked modulator cannot be overemphasized, since they must be thermally stable, mechanically robust, and electrically conducting relative to the NLO layer at the poling temperature (in this case, 310 °C). Efforts to identify appropriate buffer layers for very high temperature poling (>300 °C) are in progress.

The stability of the induced polar order in PI-1 is extraordinary for a thermoplastic NLO polymer. Figure 3 shows the ramped decay for samples prepared both from the poly(amic acid) (PAA-1) and from the chemically imidized material (PI-1). The orientational stability of the polyimide derived by thermal imidization of the poly(amic acid) PAA-1 seems to track the final cure temperature (Figure 3A,B). That of the chemically imidized sample (PI-1) is higher, presumably because the maximum poling temperature exceeded 300 °C. Other than the point at zero time, no data points were measured for curve C in Figure 3 until the sample temperature reached ~220 °C. Beyond this temperature, each data point represents a signal average from

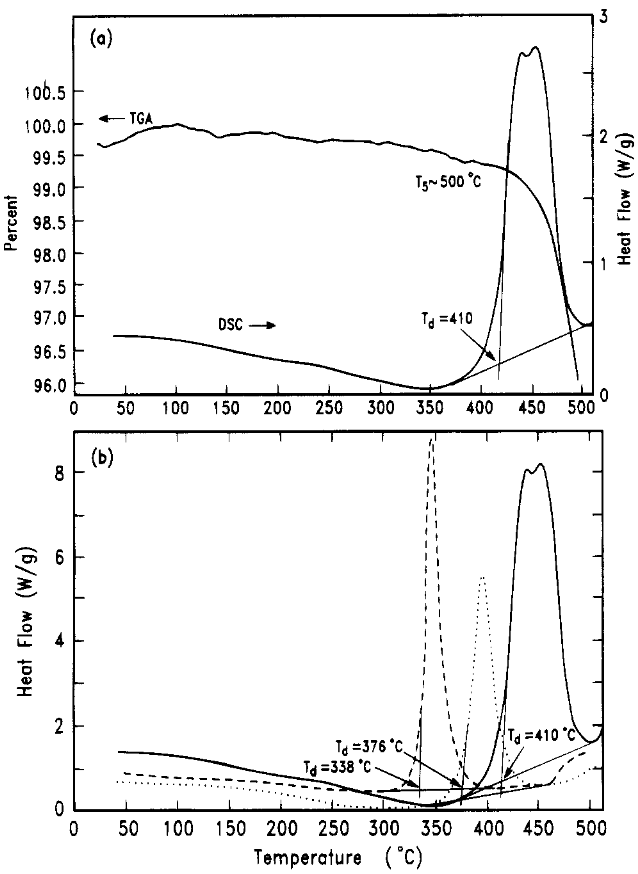


Figure 1. (a) TGA and DSC analyses of PI-1 (20 °C/min). (b) Comparative DSC analyses of PI-I (—), PI-2 (- - -), and PI-3 (• • •).

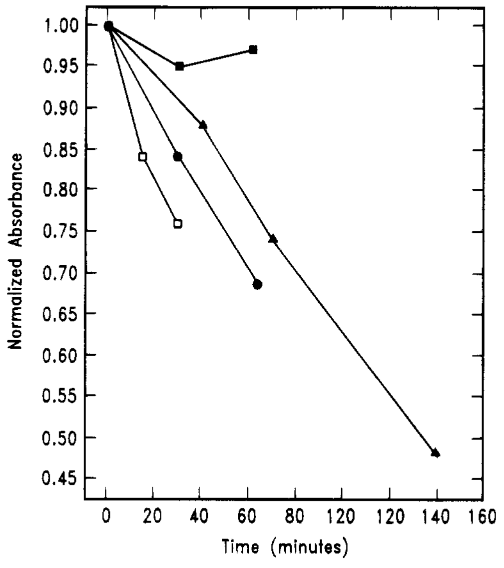


Figure 2. Variable-temperature UV–visible studies at the long wavelength: (■) PI-1 (350 °C, λ_{max} 470 nm); (□) PI-1 (377 °C); (●) PI-2 (275 °C, λ_{max} 474 nm); (▲) PI-3 (300 °C, λ_{max} 498 nm). Temperatures were measured with a thermocouple directly attached to the quartz substrate.

100 laser shots. For curves A and B, each data point represents a signal average from 1000 laser shots. Preliminary studies of the isothermal polar order stability of PI-1 at 225 and 250 °C are shown in Figure 4. The decay curves for the normalized second harmonic coefficients can be adequately fit using a standard stretched exponential expression.[4] At 225 °C, the decay is extremely slow and the extrapolated characteristic relaxation time (τ) is hundreds of years. At 250 °C, the calculated relaxation time (τ) is estimated as 75 days. Preliminary experiments suggest that the polar order stability can be further improved by aging at elevated temperatures. The extraordinary stability of the induced polar order is apparently due, in part, to the very high T_g of the system and the need to move substantial segments of the main chain in the relaxation of the chromophore.

In summary, we have prepared a soluble NLO substituted polyimide derivative containing no flexible group where the donor head is embedded in the polymer main chain. As a result of the rigidity imparted by this mode of chromophore attachment, a very high glass temperature is realized. The glass transition temperatures of polyimides containing M1 are adjustable by a judicious selection of the dianhydride component. PI-1 can be poled (corona or electrode) at high temperatures and the relaxation rate is extraordinarily slow. This material validates the potential of high-T_g NLO thermoplastic materials for high-temperature poled polymer applications and provides an alternative approach to the production of highly stabilized poled polymers which does not require extensive cross-linking and network formation.

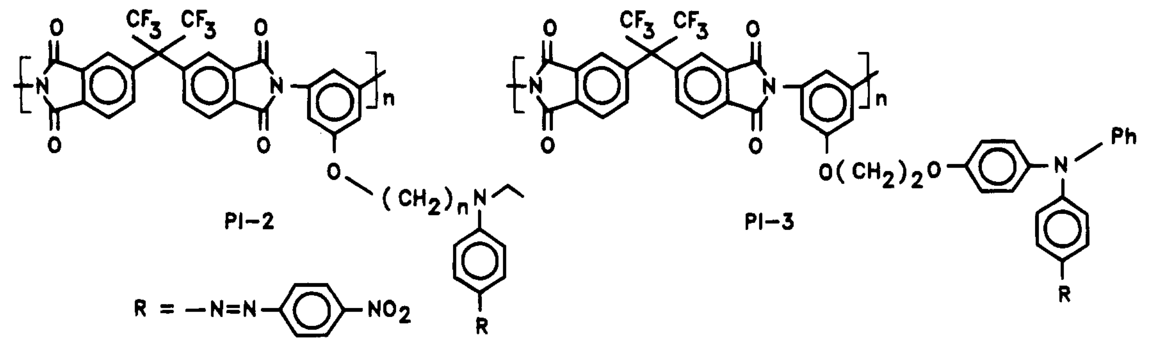
Experimental Section

^{1}H NMR and ^{13}C NMR were recorded on an IBM-Bruker AF-250 machine operating at 250 MHz for proton and 62.9 MHz for carbon and the chemical shifts are referenced relative to TMS. The fluorine NMR spectra were recorded on an IBM AC-300 machine operating at 282.4 MHz and are referenced relative to fluorotrichloromethane. IR spectra were measured using an IBM IR/32 Fourier transform instrument. The UV–visible spectra were recorded using a Hewlett-Packard 8452 A diode array instrument. The thermal gravimetric analyses and differential scanning calorimetry studies were conducted using a Perkin-Elmer TGA-7 thermogravimetric analyzer and a DuPont Instruments Inc. Model 910 differential scanning calorimeter, respectively. The GPC analyses were performed using a Waters 150-C instrument with a refractive index detector and Styragel columns and the sample molecular weights are referenced relative to polystyrene standards. The elemental analyses were performed by Galbraith Microanalytical Laboratory, Knoxville, TN.

Nonlinear Optical Measurements. The r values of the polymeric samples were measured using the ellipsometric method described in refs 23 and 24. The index of refraction of the NLO polymeric film was modulated by a small sinusoidal voltage applied to two parallel electrodes. One electrode is transparent indium tin oxide (ITO) and the other is a highly reflecting gold electrode. The laser light (1305 nm, polarized at 45° with respect to the plane of incidence) from a diode laser was launched at an angle of 30° through the transparent ITO electrode and the NLO polymer film and reflected from the gold electrode. The reflected beam is passed through a Soleil–Babinet compensator and analyzer and detected by a photodiode. The Soleil–Babinet compensator was adjusted to bias the optical system in a linear modulation regime which occurred near half the maximum detected reflected intensity. The modulation of the output intensity was detected by a lock-in amplifier. In the calculation of r_{33}, we have assumed an r_{33}/r_{13} ratio of 3 as is commonly done. Depending on the system, this is not always the case,[4,26] and significant deviations from this value may affect the accuracy of the r_{33} measurement.

The dynamic stability of the induced polar order was studied by heating the sample at a constant rate of 3 °C/min over the temperature range while monitoring the decrease in the second harmonic signal from a YLF laser operating at 1.047 μm. Isothermal polar decay was monitored by the decrease in the second harmonic signal arising from a 1.047 μm fundamental input.

Chart 1



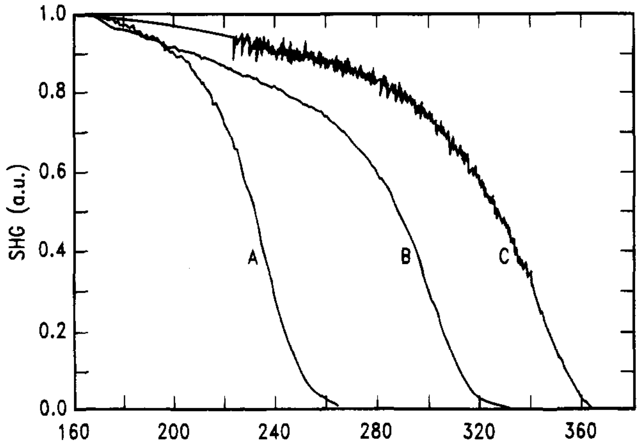


Figure 3. Polar order stability as determined by thermal ramping (rate 3 °C/min); laser fundamental 1.047 μm): (A) film prepared from the poly(amic acid) (PAA-1) heated to a maximum temperature of 250 °C in a corona field; (B) film prepared from the poly(amic acid) (PAA-1) heated to a maximum temperature of 280 °C in the corona field; (C) chemically imidized film of PI-1 poled at 310 °C (corona field).

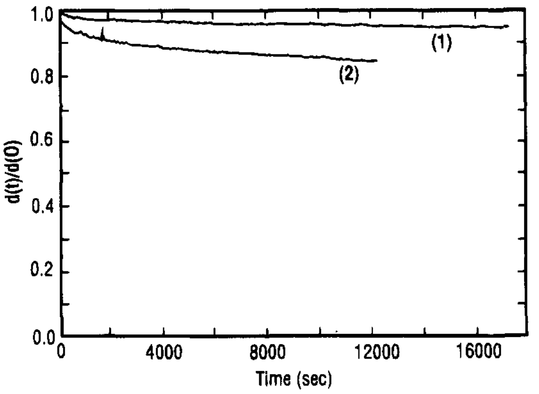


Figure 4. Relaxation of poled samples of PI-1 at elevated temperatures: **1** (225 °C, $\tau \sim$ centuries); **2** (250 °C, $\tau \sim$ 75 days).

Tris(*p*-aminotriphenyl)amine (2). Tris(*p*-nitrophenyl)amine (**1**) (2 g, 7.3 mmol, 95%) was slurried in 250 mL of dimethylformamide (DMF) and placed in a Parr pressure bottle with 250 mg of 10% Pd/C. The mixture was hydrogenated with shaking at 47 psi for 24 h. The color of the solution changed from yellow to colorless. The mixture was filtered through Celite and poured into 500 mL of water with stirring. The gray precipitate was filtered and dried in vacuo (1.4 g, 66%). The solid was dissolved in 150 mL of hot ethanol and filtered after cooling to yield gray, shiny crystals: mp 241–244 °C, lit.[27] ^{1}H NMR (acetone-d_6) δ 6.70 (AB q, J = 7.5 Hz, 6H), 6.52 (AB q, J = 7.5 Hz, 6H), 4.31 (br s, 6H); ^{13}C NMR (acetone-d_6) δ 143.6, 140.5, 125.1, 115.8.

Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.29. Found: C, 74.10; H, 6.36; N, 18.90.

4-(*N*,*N*-Bis(*p*-aminophenyl)amino)-4′-nitroazobenzene (M1). *p*-Nitrosonitrobenzene[28] (1.83 g, 12 mmol) was dissolved in 50 mL of warm acetic acid and cooled to room temperature. To the solution was added 6.09 g (21 mmol) of tris(*p*-aminophenyl)amine (**2**), and the reaction was stirred for 3 h at room temperature. The reaction mixture was poured into 200 mL of 20% potassium carbonate solution containing 150 mL of ethyl acetate which was cooled in ice. The mixture was filtered through Celite, and the layers were separated. The aqueous layer was extracted with 150 mL of additional ethyl acetate, washed with water, and dried over Na_2SO_4. After evaporation, the residue was purified by flash column chromatography with ethyl acetate–hexane (gradient elution 20–60% ethyl acetate). The purple product was isolated by filtration (2.87 g, 56%) and recrystallized from 350 mL of hot toluene to yield 2.67 g of product: mp 240–241 °C; ^{1}H NMR (DMSO-d_6) δ 8.32 (d, J = 7.5 Hz, 2H), 7.91 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 6.95 (d, J = 7.5 Hz, 4H), 6.65 (d, J = 7.5 Hz, 2H), 6.59 (d, J = 7.5 Hz, 4H), 5.21 (s, 4H); ^{13}C NMR (THF-d_8) δ 155.7, 152.9, 146.6, 145.7, 143.9, 134.2, 126.8, 124.2, 123.4, 121.4, 114.9, 113.8; IR (KBr) 3400, 1605, 1586, 1509, 1430, 1390, 1382, 1300, 1280, 1190, 1133, 1103, 840, 800 cm^{-1}.

Anal. Calcd for $C_{24}H_{20}N_6O_2$: C, 67.91; H, 4.95; N, 19.80. Found: C, 67.75; H, 4.88; N, 19.50.

Preparation of PI-1. (**A**) A 20 mL vial was charged with 1.051 g (2.476 mmol) of diamine (M1) and 8 g of freshly distilled, dry *N*-methylpyrrolidone (NMP). The mixture was stirred magnetically until complete dissolution of the diamine was achieved, and then 1.100 g (2.476 mmol) of (hexafluoroisopropylidene)diphthalic anhydride (6FDA) was added and washed in with another 4 g of NMP. The polymerization mixture was then stirred for 48 h, yielding a dark red, highly viscous poly(amic acid) solution (PAA-1).

(B) Chemical Imidization of the Above Poly(amic acid). A 7.5 g sample of the above solution, 15.2 wt %, was treated with 0.79 g (10 mmol) of dry pyridine and 1.02 g (10 mmol) of acetic anhydride. The mixture was stirred for approximately 16 h at ambient temperature and finally at 60–70 °C for an additional 6 h. The resulting polyimide solution was then precipitated into deionized water with vigorous stirring and thoroughly extracted, first with methanol and finally with ethyl acetate. The dark powder was then dried in vacuo at 65 °C for 24 h, providing 1.01 g (92.7%) of the desired polyimide: GPC (THF) M_w = 174 699, M_n = 79 206; ^{1}H NMR (THF-d_8) δ 8.35 (d, J = 9.1 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H), 7.8–8.05 (m, 8H), 7.5 (d, J = 8.8 Hz, 4H), 7.38 (d, J = 8.8 Hz, 4H), 7.28 (d, J = 9.1 Hz, 2H); ^{13}C NMR (THF-d_8) δ 164.6, 155.1, 150.5, 147.5, 146.6, 144.9, 137.4, 134.8, 132.3, 131.9, 126.9, 125.0 (J = 288 Hz), 124.7, 124.1, 123.6, 122.7, 121.0, 64.4 (J = 29.2 Hz); IR (KBr) 1786, 1722, 1628, 1502, 1382, 1338, 1319, 1312, 1212, 1187, 1136, 1099, 864, 833, 763, 739, 720 cm^{-1}; ^{19}F NMR (THF-d_8) δ −62.5 (relative to $CFCl_3$ standard).

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