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Synthesis of Hydroxymethyl-Functionalized Polyimides and the Facile Attachment of an Organic Dye Utilizing Bis(isocyanates) and Bis(acid chloride) Linkers

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ABSTRACT: Two new monomers were prepared of the formula 3,*X*-bis(4-aminophenoxy)benzenemethanol (where $X = 5$, **3a**; $X = 4$, **3b**) and each copolymerized with 2,2-bis(4-aminophenyl)hexafluoropropane, 6-FDA, and 6 mol % of phthalic anhydride as an end-cap to afford polyimides **4** and **5**, respectively. The CH_2OH group in the polymers could be modified with excess 1,6-hexanediisocyanate to afford 100% modification of polymer **6** concomitant with formation of a pendent and reactive isocyanate group. This latter polymer was shown to react with disperse red 1 (DR-1) to produce a polyimide-supported dye (**7**, T_g 199 °C) via formation of a urethane linkage. Treatment of the polymers **4** and **5** with excess adipoyl chloride afforded polymers **8** and **9**, respectively, with a pendent acid chloride functional group. Further reaction with disperse red 1 (DR-1) in the presence of DMAP led to rapid esterification, yielding high-T_g dye-attached polyimides **11** (T_g 168 °C) and **12** (T_g 175 °C). Treatment of polymer **4** with sebacoyl chloride (a longer spacer) and then DR-1 in a similar manner afforded polymer **13** (T_g 156 °C). All dye-attached polymers showed low optical loss as measured in solution at both 1300 (∼0.5 dB/cm) and 1500 nm (∼1.0 dB/cm) and showed excellent thermal stability at an elevated temperature (180 °C) relative to guest/host analogues.

Introduction

The chemical modification and use of fluorinated polymers plays a key role in a variety of today's advanced materials technologies.[1] The practice of post-polymer modification ranges dramatically in purpose and style. We continue to see elegant applications of post-polymer modification in diverse areas of polymer chemistry that include approaches to combinatorial synthesis[2] and the development of novel electro- and optoactive materials with conjugated polymer backbones.[3]

More specifically, we have had interest in developing a strategy for the efficient and chemically mild incorporation of organic dyes into a robust polymeric material. There are currently two principal means of attaching an organic dye to a polymer. One method is to prepare a monomer containing the optoactive group and then co- or homopolymerize the molecule.[4] This requires the optoactive group to be stable to the polymerization conditions and any other post-cure processes. The other method is to link (i.e., chemically bond) a suitably functionalized optoactive molecule to an existing polymer backbone.[5] The two methodologies have clear advantages and disadvantages related to (1) chemical efficiency (e.g., number of synthetic steps) and (2) functional group tolerance.

With interest in utilizing polyimides (PIs) as the bulk polymeric material, we found relatively few synthetic procedures that provide a mild and efficient means of attaching a dye to the polyimide backbone.[5,6] In addition to having mild reaction conditions and high attachment efficiency, we sought synthetic methodology that would permit systematic changes in T_g and isolation of the dye from the backbone structure. Very recently, Luo and coworkers[7] reported on the modification of a phenolic−polyimide backbone by use of a diacid linker and two consecutive esterification steps. In that case, ∼50% of the potential dye sites (i.e., backbone phenolic −OH's) were utilized. In this paper we present a very chemically efficient and versatile synthetic route for the attachment of organic dyes to a polyimide backbone based on the modification of a benzylic alcohol sites that affords materials possessing low optical loss and high T_g's.

Results and Discussion

Monomer Synthesis. From the readily available methyl 3,5-dihydroxybenzoate we have developed a very efficient synthetic scheme for the preparation of the new monomer 3,5-bis(4-aminophenoxy)-1-hydroxymethylbenzene (**3a**) (Scheme 1).[8] We find that **1a** can be quickly purified by trituration with hot ethanol. The remaining two steps are performed in such a manner as to require only simple filtrations to afford analytically pure samples. It is interesting to note in the hydrogenation of **1a** that completion of the reaction is signaled by a visually distinct agglomeration of the catalyst.

The synthesis of monomer intermediate **1b** proves to be more difficult and time-consuming. The primary difficulty is reaction of the 4-fluoro-1-nitrobenzene at the 3-position of the methyl benzoate compound after the initial and faster reaction at the 4-position. Column chromatography is utilized to remove the methyl 3-hydroxy-4-(4-nitrophenoxy)benzoate byproduct from the desired product. The structure of the latter compound is easily verified by proton NMR spectroscopy. Once **1b** was in hand, the remaining two steps proceed in excellent yield and ultimately provide the monomer **3b** in 50% overall yield.

Polymer Synthesis and Dye Attachment. Monomers **3a** and **3b** are each copolymerized with 2,2-bis(4-aminophenyl)hexafluoropropane and hexafluoroisopropylidene-2,2-bis[4-phthlaic anhydride] (6-FDA) to afford polyimides **4** and **5**, respectively. The functionalized monomers are used in a molar ratio that affords a final

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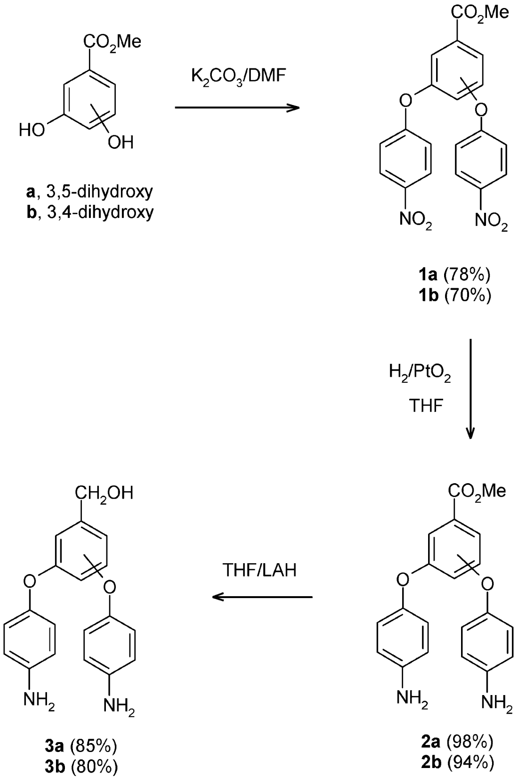
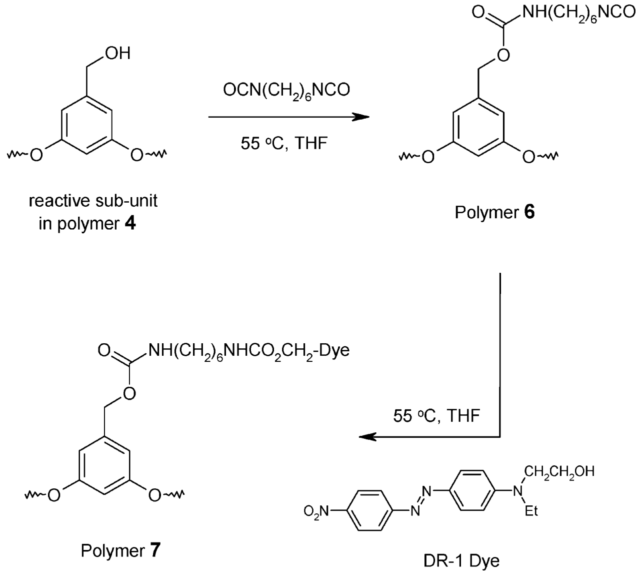
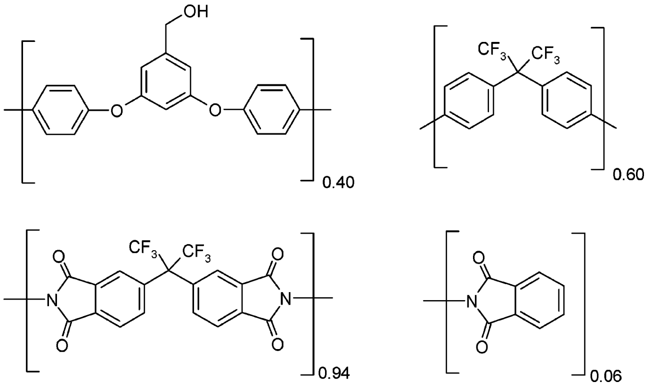
Scheme 1



Scheme 2



polyimide having ~0.6 mequiv of −OH per gram of polymer. In addition, all polymerizations are carried out using 6 mol % of phthalic anhydride as end-cap to provide control over molecular weight. Under the present polymerization conditions, we obtain polymers with number-average molecular weights in the range of ~5500 to ~6500 and polydispersities of ~2. Polyimides **4** and **5** are found to have T_g's of 268 and 283 °C, respectively. These are typical of polyimides and fall into a very useful range for many photonic-type applications. The polymers are soluble in common organic solvents, although we observe best solubility (20 wt % or more) in oxygenated solvents such as THF and *p*-dioxane.



Complete assignment of the proton NMR data for polymers **4** and **5** has been completed and is placed in the Experimental Section. In each case the benzyl methylene is well separated from other NMR signals and proves to be a valuable diagnostic probe for the subsequent polymer modification chemistry presented herein.

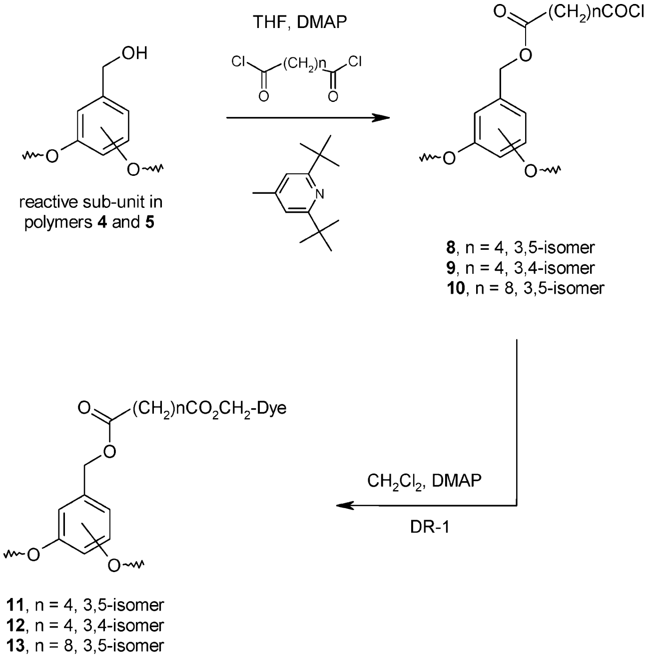
We have explored two new approaches for the attachment of dye molecules to a polyimide backbone. In each strategy, we sought to attach a functional group that would react with an alcohol group under mild reaction conditions at or near neutral pH. It is imperative to avoid the use of nucleophilic agents or harsh reaction conditions that might decompose some of the more sensitive dyes that are in current use. In addition, to retain good polymer properties and processability the modification chemistry must avoid cross-linking and/or backbone scission reactions.

The first approach involved treatment of **4** with an excess (~30-fold) of 1,6-diisocyanatohexane in the presence of triethylamine (Scheme 2). Complete reaction at the benzyl alcohol group in polymer **4** is evident in the proton NMR spectrum. The benzyl-methylene NMR signal shows a downfield shift of nearly 0.5 ppm upon conversion to the urethane. The pendent isocyanate in polymer **6** is observed in the IR spectrum as a strong absorbance peak at ~2271 cm^{-1}. The polymer retains excellent solubility in THF, hence suggesting that little if any cross-linking has occurred during polymer modification.

Polymer **6** does undergo reaction with the alcohol functional group of DR-1 in the presence of DMAP to afford polymer **7**. Although NMR data show better than 90% attachment efficiency (i.e., comparison of the benzyl methylene to the dye-CH_2OCNH− signals), there is evidence in the infrared spectrum of polymer **7** for unreacted isocyanate groups. This is evidenced by an infrared absorption at 2265 cm^{-1} that by relative integration values may account for ~5% of the starting isocyanate sites being left unreacted. Elemental analysis data for the polymer are in very good agreement with the proposed structure. Analysis of polymer **7** by SEC shows a small increase in polydispersity (2.4 ⇒ 2.8) with a concomitant decrease in retention time. These data coupled with excellent solubility are indicative that little cross-linking has occurred through the dye attachment chemistry. Although not explored in this work, the unreacted isocyanate groups may prove useful for subsequent cross-linking reactions.

The second approach to dye attachment involves treatment of polymers **4** and **5** with a 10-fold excess of a diacid chloride in the presence of 2,6-di-*tert*-butyl-4-methylpyridine and 4-(*N*,*N*-dimethylamino)pyridine (DMAP). This affords the functionalized polymers **8** and

Scheme 3



9, respectively, in high purity as determined by NMR spectroscopy and good yield (Scheme 3). In the reaction a precipitate is formed that is believed to be, in part, the pyridinium hydrochloride salt. The precipitate is removed from the reaction mixture by passing the reaction mixture through a plug of Celite. It is important to carry out the precipitation in ether and collection of the polymers under the protection of dry nitrogen. The polymers isolated after brief drying show complete functionalization of the benzyl sites (i.e., loss of the NMR signal at 4.63 ppm) with the expected proportion of pendent acid chloride sites. The proton NMR spectrum is again particularly useful for assigning the extent of chemical modification and the integrity of the pendent acid chloride functional group. Infrared spectroscopy clearly showed the carbonyl stretch for the acid chloride at 1785 cm^{-1}, which upon reaction with dye moves into the massive imide−carbonyl band.

We find that polymers **8**−**10** afford the highest and most consistent dye attachment efficiencies if used immediately after drying for a period of only 1 h at reduced pressure (~0.2 Torr). By NMR spectroscopy we can observe residual ether; however, there appears to be no interference with the dye attachment reaction. We have also found the pendent acid chloride to be extremely sensitive to choice of the acid scavenger. For example, triethylamine affords low dye attachment efficiencies with concomitant destruction of the acid chloride. At this point in time we do not have spectroscopic evidence to single out one particular pathway for decomposition. Even with low attachment efficiencies, we observe only one benzyl−CH_2O_2C− signal in the proton NMR spectrum. This would indicate that the side reaction is occurring at the acid chloride functional group and does not seem to involve the benzylic position.

In a similar manner, we have taken polymer **5** and treated it with excess adipoyl chloride and isolated the acid chloride functionalized polymer and then attached DR-1 using DMAP in dichloromethane. This process affords polymer **12** in good yield. The latter polymer only differs from **11** by the linkage substitution on the benzyl alcohol core unit.

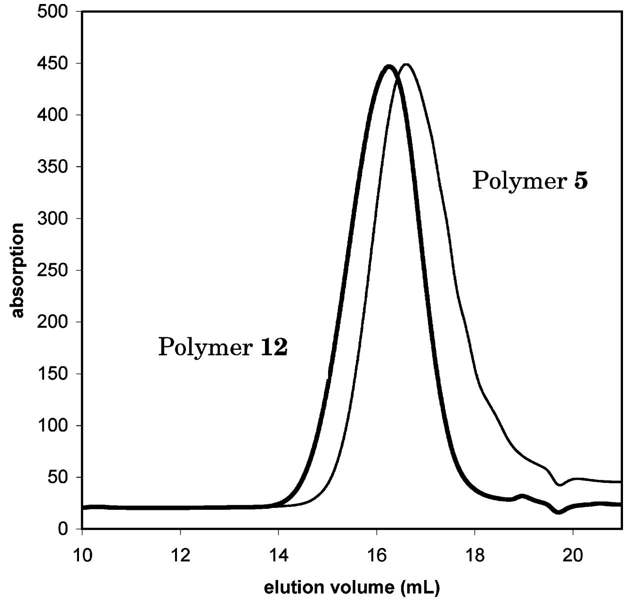


Figure 1. SEC traces for polymer **5** before chemical modification and then polymer **12** with DR-1 attached.

We have followed the polymer modification in the preparation of **12** using SEC analysis, and the results are displayed in Figure 1. These data demonstrate visually that the attachment chemistry does not modify the polydispersity of the polymer at each stage of the modification; however, it does afford the anticipated increase in molecular weight upon dye attachment.

One of clear advantages to the attachment strategy presented in this paper is the ability to tailor the length of the spacer that connects the dye to the polymer backbone. It is well-known that the length of the spacer can directly affect the ability of the NLO-phore (i.e., dye) to be oriented during an alignment process. To demonstrate this ability, we choose a diacid chloride with 10 carbons, namely sebacoyl chloride. The increased linker length leads to a DR-1 modified polymer with a significantly lower T_g of 156 °C (~20 °C in comparison to **11**).

Polymer Physical Properties and Processing. To successfully carry out the analysis of optical loss in solution and thermal stability of polymer films, it is necessary to select a common solvent for the polyimide backbone (in this study that refers to polymer **4**), free DR-1, and the chromophore-attached polymer that featured a sufficiently high boiling point to enable spin-casting of high-quality films and that has a reasonably simple absorption spectrum in the near-infrared region of interest. Of the nearly one dozen potential solvents identified, cyclohexanone was judged to best fulfill the requirements stated above.

Since sample preparation involves use of filtered solutions, it is necessary to ensure that the filtration process is not inadvertently removing significant amounts of either the polymer or the chromophore; a simple comparison of spectra using filtered and unfiltered solutions was performed over a wavelength of 500−1600 nm in order to observe the peak absorption band edge of DR-1. Both the magnitude and location of the band edge remained unchanged before and after filtration, strongly supporting the hypothesis that no DR-1 is removed during filtration.

Figure 2 shows the optical loss spectra of the chromophore-attached polyimide along with the backbone polymer and the backbone/DR-1 mixtures from 1000 to

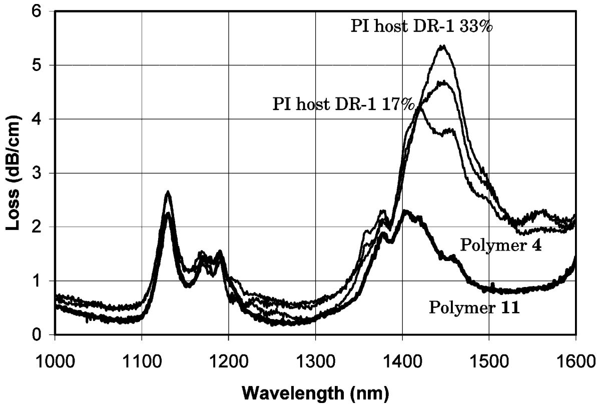


Figure 2. Optical loss, as measured by near-infrared spectroscopy, for the SC-DR-1 polymer and guest/host mixtures of the backbone and chromophore starting materials.

1600 nm. The calculated volume fractions of solute were 3.7% for the polyimide backbone, 3.8% for the 17 wt % DR-1 in polyimide and for the chromophore-attached polyimide, and 4.1% for the 33 wt % DR-1 in polyimide. The resulting density values of 1.3 g/cm^3 for the backbone polyimide, 1.25 g/cm^3 for the chromophore-attached polyimide, and 1.25 and 1.15 g/cm^3 for the 17 and 33 wt % guest/host systems, respectively, are quite reasonable. Examination of the spectra as a function of the proposed volume fraction of solute shows that the error in the volume fraction estimate is about ±0.1% or, in terms of density, about 0.05 g/cm^3. Further examination of the spectra show that the observed loss values at 1300 and 1550 nm are very insensitive to variations of the proposed volume fractions, changing by only about 0.05 dB/cm per 0.1% change in volume fraction.

For all but the chromophore-attached polymer, the spectra reveal two distinct trends. At wavelengths below 1400 nm, the losses are highest for the backbone polyimide and decrease with increasing DR-1 content. These samples show broad regions where no significant absorption peaks are present at 1000−1100 and 1240−1320 nm, in which the losses range from 0.5 to 0.7 dB/cm for the polyimide backbone to 0.2−0.4 dB/cm for the backbone with 33 wt % DR-1. Thus, neither the polyimide nor the DR-1 is likely to cause significant loss issues in these regions.

For wavelengths in excess of 1400 nm, however, the trend is reversed. Of the backbone and guest/host systems, the polyimide with no DR-1 shows the lowest losses, while increasing DR-1 leads to increased loss, especially in the regions of strongest absorption around 1450 nm. At 1550 nm, the losses range from just under 2 dB/cm for the backbone to near 2.3 dB/cm for the 33 wt % DR-1 system. Thus, at these wavelengths, optical losses from the starting materials for the chromophore-attached polymer are potentially troublesome. When the losses from the chromophore-attached polymer itself are considered, however, the differences between wavelengths above and below 1400 nm become even more apparent. Below 1400 nm, the chromophore-attached polymer behaves similarly to the guest/host systems, with a very low loss of 0.3 dB/cm at a wavelength of 1300 nm. Above 1400 nm, however, the losses in the chromophore-attached polymer are significantly lower than in the guest/host systems, with a broad region free of absorption peaks between about 1480 and 1560 nm, in which the loss is just 0.8−1.0 dB/cm. The losses for the chromophore-attached polymer are thus as low or lower than those of the starting materials. Moreover, the losses of the chromophore-attached polyimide are quite similar to those of other polyimides measured in our laboratory[9] and to other well-known host polymers for optical applications, such as amorphous polycarbonate.[10]

The most likely explanation for the unusually high loss values in the backbone polyimide and guest/host polymer systems above 1400 nm is the presence of hydroxyl groups on both the DR-1 and on the backbone itself (i.e., polymer **4**). Whereas in the backbone, there is one hydroxyl group per ~1600 amu equivalent weight; in DR-1 there is one hydroxyl group per 314 amu equivalent weight. Thus, if hydroxyl groups were the major constituent of the excess optical loss, then loss should increase with increasing DR-1 content in guest/host systems; however, it should be greatly reduced as the attachment reaction consumes both DR-1 and backbone hydroxyl groups.

Perhaps the most important conclusion that can be drawn from the absorption data is that the completion of the attachment reaction is seen to introduce no major sources of absorption into the near-infrared spectrum. The only clearly visible "new" peaks that coincide with the completion of attachment appear in the 1150−1200 nm range and are small. Moreover, the measured losses for the chromophore-attached polymer are generally at or below about 0.5 dB/cm at 1300 nm and 1 dB/cm at 1500 nm. Although these results apply only to "intrinsic" absorption in solution and a technique such as photothermal deflection spectroscopy[11] would be needed to make definitive statements about solid-state behavior, the presence of broad regions free of major absorption peaks in the solution spectrum of the chromophore-attached polymer is a very positive indicator for low loss behavior in solid-state films.

Thermal Stability of the Dye-Modified Polyimides. While avoiding increased optical losses is an important achievement in developing chromophore attachment reactions, by itself it does not demonstrate that a chromophore-attached polymer system would be any more desirable than the equivalent guest/host system for electrooptical applications. It is therefore important to validate that the chromophore-attached materials do indeed deliver at least some of their promised benefits. These include but are not limited to increased physical thermal stability of the chromophore, restricted motion (especially below T_g), and a decrease in tendencies for phase separation (i.e., crystallization or aggregation of the dye).

Although it is possible to perform dynamic nonlinear optical thermal stability measurements on poled electrooptical devices to test the effects of chromophore attachment on inhibiting the free motion of the chromophore molecules, a much simpler test involves the linear optical stability of very thin films. Many guest/host systems, including those containing DR-1, are known to suffer from unwanted sublimation of the chromophore molecules at elevated temperatures.[12] This effect is easily measured by examining the absorption spectrum of DR-1 in submicron-thick films as a function of time at elevated temperatures, where it is found that when sublimation takes place, there is a rapid loss in absorption intensity over a periods as short as a few minutes. Figure 3 shows the relative decrease in absorption intensity (at the peak absorption wavelength)

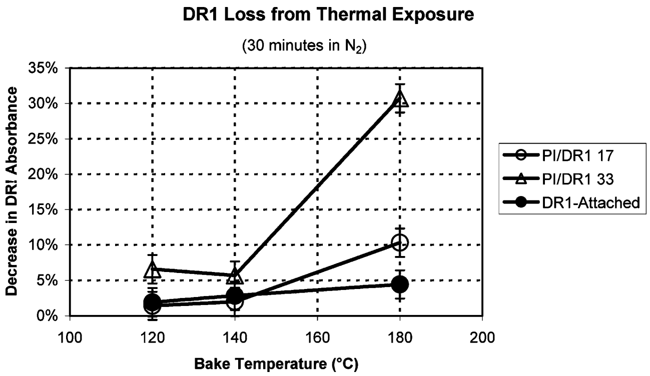


Figure 3. Relative amounts of chromophore lost to sublimation or degradation after exposure to elevated temperature for the SC-DR-1 polymer and guest/host mixtures of the backbone and chromophore starting materials.

for film ranging in thickness from 0.3 to 0.6 μm of the chromophore-attached DR-1 polymer and two corresponding guest/host systems having 17 and 33 wt % DR-1, respectively, after being exposed to various temperatures for a period of 30 min. The general trend at all temperatures is for the 33 wt % guest/host system to suffer the largest changes, followed by the 17 wt % guest/host system and, last, by the chromophore-attached polymer. The differences are most pronounced at 180 °C, where the chromophore-attached polymer's peak absorption changes by just over 4%, compared to over 10% for the 17 wt % guest/host system and over 30% for the 33 wt % guest/host system.

The loss of absorption intensity in these systems at elevated temperature could be due to any one or a combination of three likely causes: (1) changes in the absorption spectrum of the host (or backbone) polyimide, (2) sublimation of DR-1, or (3) chemical degradation of DR-1. To check the first possibility listed above, the spectrum of the polyimide host (which is also the backbone for the dye-attached polymer) was compared before and after exposure to 180 °C for 30 min. The observed spectral changes were negligible, indicating that the backbone polyimide is very stable, as expected, at these temperatures. Distinguishing between the second and third possibilities is more difficult, but DR-1 is not known to suffer significant chemical degradation in a nitrogen atmosphere at 180 °C, and, if it were, we would expect such degradation to affect the chromophore-attached and guest/host systems to a similar extent. Thus, although a small portion of the loss in absorption, particularly in the chromophore-attached polymer may be attributed to degradation, the major component of the differences between the guest/host and chromophore-attached systems must be ascribed to differences in the sublimation rate of DR-1.

In comparing the guest/host and chromophore-attached systems, it is also worth noting that the rate of sublimation (relative to the initial amount of chromophore present) should increase with decreasing film thickness if diffusion of the chromophore within the film is a limiting factor in mass transfer. In our case, the thinnest film, at 0.3 μm, was the chromophore-attached polymer, followed by the 17 wt % guest/host system at 0.45 μm and the 33 wt % system at 0.6 μm. Thus, if the effects of film thickness were significant, they would only serve to mask the intrinsic differences among the systems studied by reducing the rate of guest/host chromophore sublimation relative to that in the attached chromophore polymer. Hence, it is quite clear a significant reduction in chromophore mobility has been achieved by the chemical attachment, and this new attachment chemistry is quite stable at high temperatures for extended periods of time.

Concluding Remarks

In this work we have demonstrated that a benzyl alcohol-functionalized diamine can be polymerized with bis(anhydrides) to a highly functionalized polyimide that exhibits exceptional solubility and processability. Furthermore, we have shown that the benzyl alcohol group in the new polymers can be chemically modified with a bis-functional linking agent, for example bis(isocyanates) or bis(acid chlorides), to afford reactive side-chain polyimides that contain a reactive isocyanate or acid chloride group. The "pendent functional" group has been shown to provide an excellent site for attachment of an alcohol-containing dye (like DR-1). Furthermore, by changing the length of the linker (i.e., diacid chloride), a means of tuning the polymers final T_g is possible with this new attachment chemistry. The polyimides presented here with DR-1 attached were shown to have excellent thermal properties as well as low optical loss. Work continues to more fully utilize the full potential of this very efficient attachment/polymer modification chemistry.

Experimental Section

General Synthetic Methods. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Tetrahydrofuran (THF), ether, *N*-methylpyrrolidinone (99.5%), and dichloromethane solvents were purchased as the anhydrous grade and inhibitor-free from Aldrich and used as received. ^1H and ^{13}C NMR measurements were performed using a Bruker AC 200 or Bruker Avance 400 MHz instrument. ^1H and ^{13}C NMR chemical shifts are reported vs the deuterated solvent peak (solvent, ^1H, ^{13}C: $CDCl_3$, δ 7.27 ppm, δ 77.0 ppm; DMSO-d_6, δ 2.50 ppm, δ 39.5 ppm). Methyl 3,5-dihydroxybenzoate, 4-fluoronitrobenzene, LAH (95%, powder), cyclohexanone (99+%), and phthalic anhydride were purchased from Aldrich Chemical Co. and used as received. The 6-FDA (lot #104\65) and 6F-4,4′-diamine were purchased from CHRISKEV Co. and used as received. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA.

Optical Loss Measurements. The guest/host systems were mixed by adding enough solvent to 5:1 and 2:1 by weight mixtures of the backbone polyimide and the DR-1 to make 5 wt % solutions (for spectrophotometry) or 10 wt % solutions (for film casting) and stirring vigorously at room temperature for 2 h. Corresponding solutions of only the polyimide backbone and only the chromophore-attached polymer were similarly prepared. Unless otherwise noted, all solutions were passed through Teflon filters (pore size 0.2 μm) prior to use.

Optical measurements were carried out in a Cary 5 spectrophotometer using quartz cuvettes following a previously published procedure.[9] With these careful procedures in place, a precision of 0.0005−0.001 in absorbance could be obtained, which translated into around ±0.2 dB/cm in solution optical loss.

Thermal Stability Studies. Solutions in cyclohexanone at 10 wt % were prepared of the chromophore-attached polymer, the backbone polyimide, and guest/host mixtures of the backbone polyimide and DR-1 in a 5:1 and 2:1 weight ratio, which are referred to as the 17 and 33 wt % mixtures, respectively. The solutions were filtered and then spun onto clean glass microscope slides at 2400 rpm for 30 s using a Headway Research, Inc., model EC101 spin-casting apparatus. The resulting films were baked at 70 °C for 30 min under dry nitrogen and then allowed to sit at room temperature for another 24 h. This procedure is known to be effective for removing practically all cyclohexanone from the resultant films, which ranged in thickness from 0.3 to 0.6 μm.

After the initial drying was complete, a spectrum of the film was recorded from 800 to 350 nm at 0.6 nm intervals and an averaging time of 0.1 s, with the spectrum of an uncoated but similarly cleaned microscope slide as a baseline. The film was placed in the spectrophotometer beam in a sample holder that allowed for accurate control of the beam location on the surface of the film. After collecting the spectrum, the sample was again heated for 30 min under dry nitrogen. Separate samples were used with heating temperatures of 120, 140, and 180 °C. After heating, the samples were quickly cooled to room temperature, aligned in the sample holder so that the same location would be illuminated by the sample beam, and measured again using the same procedure. The spectra of the samples (except for the backbone polyimide with no DR-1) consisted of a single, large peak of absorbance 0.8−2.4 at 475−500 nm. Although the spectrum of the backbone polyimide showed a small absorbance at this wavelength, its effect on the relative change in the value of the peak absorbance was considered negligible. Thus, the amount of DR-1 lost during the exposure to high temperature was computed on the basis of the relative peak absorption between 475 and 500 nm as compared before and after exposure. The error in the measured peak values has been demonstrated to be around 1%, which is easily small enough to allow for the desired comparisons.

Preparation of Methyl 3,5-Bis(4-nitrophenoxy)benzoate (1a). A flask was charged with methyl 3,5-dihydroxybenzoate (23.0 g, 137 mmol), DMF (200 mL), K_2CO_3 (65 g, 0.471 mol), and 4-fluoronitrobenzene (32 mL, 260 mmol), in that order. The mixture was heated at ~60 °C for a period of 48 h with stirring. The mixture was diluted with dichloromethane (500 mL) and washed several times with water (5 × 300 mL) in an Erlenmeyer flask with vigorous stirring. The organic layer was washed with brine (100 mL) and then dried over $MgSO_4$. The solvents were removed under reduced pressure, and the crude product was triturated using hot ethanol (~100 mL) to afford light yellow crystals of **1a** (43.6 g, 78%, mp 176−179 °C).

Preparation of Methyl 3,5-Bis(4-aminophenoxy)benzoate (2a). A Schlenk flask was charged with methyl 3,5-bis-(4-nitrophenoxy)benzoate (10.0 g, 24.4 mmol), THF (150 mL), and platinum oxide (800 mg). The mixture was placed under a hydrogen atmosphere (~2 psig) and allowed to react with stirring for 6−10 h. At the end of the reaction the platinum oxide catalyst is seen to aggregate at the bottom of the flask, signaling completion of the reaction. The mixture is filtered through a plug of Celite and the THF removed under reduced pressure to afford pure methyl 3,5-bis(4-aminophenoxy)benzoate as a white powder (8.40 g, 98%, mp 159−161 °C, lit.[8] 165−167). ^{1}H NMR (DMSO-d_6) δ: 6.94 (d, J = 2.4 Hz, 2 H), 6.80 (d, J = 8.8 Hz, 4 H), 6.70 (t, J = 2.4 Hz, 1 H), 6.61 (d, J = 8.8 Hz, 4 H), 5.06 (br s, 4 H, NH_2), 3.75 (s, 3 H, OCH_3).

Preparation of 3,5-Bis(4-aminophenoxy)benzene Methanol (3a). A THF (200 mL) solution containing methyl 3,5-bis(4-aminophenoxy)benzoate (8.40 g, 24.0 mmol) was added dropwise to a THF (200 mL) solution/suspension containing LAH (4.10 g, 108 mmol). A gentle reflux was maintained during the addition as well as controlling evolution of hydrogen gas. After complete addition of the ester solution, the mixture was heated at reflux under a nitrogen atmosphere for an additional 18 h with stirring. The mixture was carefully quenched with water (4.1 mL), 15% aqueous NaOH (4.1 mL), and water (12.3 mL) and then dried over magnesium sulfate (~2 g). The solution was filtered, and the THF was removed under reduced pressure to afford pure monomer **3a** (as an oil, which after standing, may crystallize, 6.58 g, 85%, mp 97−99 °C). The yield is adjusted for the sample containing 0.1−0.3 mol equiv of THF as determined by proton NMR spectroscopy. ^{1}H NMR (DMSO-d_6) δ: 6.75 (d, J = 8.7 Hz, 4 H), 6.59 (d, J = 8.7 Hz, 4 H), 6.42 (d, J = 2.2 Hz, 2 H), 6.23 (t, J = 2.2 Hz, 1 H), 5.15 (br s, 1H, OH), 4.96 (s, 4H, NH_2), 4.35 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6) δ: 160.1, 145.7, 145.6, 145.2 (aromatic C's), 121.0, 114.8, 107.3, 103.2 (aromatic CH's), 62.5 (CH_2). Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.83%; H, 5.63%; N, 8.69%. Found: C, 70.81%; H, 5.89%; N, 8.62%.

Preparation of Methyl 3,4-Bis(4-nitrophenoxy)benzoate (1b). A flask was charged with methyl 3,4-dihydroxybenzoate (5.00 g, 29.7 mmol), DMF (50 mL), K_2CO_3 (13 g, mmol), and 4-fluoronitrobenzene (9.22 g, 6.93 mL, 65.3 mmol), in that order. The mixture was heated at ~70 °C for a period of 48 h with stirring. The mixture was diluted with dichloromethane (200 mL) and then water (400 mL). This mixture was stirred vigorously for 15 min, and the layers were separated. The organic layer was washed in this manner with water (4 × 100 mL) and brine (100 mL) and then dried over magnesium sulfate. The drying agent was removed, and the solvents removed under reduced pressure. Final purification was achieved by column chromatography (2 × 20 cm, silica gel, hexanes/dichloromethane, 1/4, v/v, respectively). The product was the second major band collected off the column and after removal of the solvents afforded **1b** as a light-yellow glassy-like solid (8.52 g, 70%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 8.05 (d, J = 7.0 Hz, 2H), 8.04 (d, J = 7.0 Hz, 2H), 7.90 (dd, J = 2.0, 8.5 Hz, 1H), 7.82 (d. J = 2.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 6.85 (d, J = 7.0 Hz, 2H), 6.81 (d, J = 7.0 Hz, 2H), 3. 81 (s, 3H, OCH_3). Anal. Calcd for $C_{20}H_{14}N_2O_8$: C, 58.54%; H, 3.44%. Found: C, 58.70%; H, 3.50%.

Preparation of Methyl 3,4-Bis(4-aminophenoxy)benzoate (2b). A Schlenk flask was charged with methyl 3,4-bis-(4-nitrophenoxy)benzoate (3.50 g, 10.0 mmol), THF (75 mL), and platinum oxide (350 mg). The mixture was placed under a hydrogen atmosphere (~2 psig) and allowed to react with stirring for 12 h. At the end of the reaction the platinum oxide catalyst is seen to aggregate at the bottom of the flask. The mixture was filtered through a plug of Celite and the THF removed under reduced pressure to afford pure **2b** as a white solid (2.82 g, 94%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.55 (dd, J = 2.0, 8.5 Hz, 1H), 7.48 (d, J = 2.0 Hz, 1H), 6.80 (d, J = 8.7 Hz, 4H), 6.75 (d, J = 8.5 Hz, 1H), 6.59 (d, J = 8.7 Hz, 4H), 3. 75 (s, 3H, OCH_3), 3.53 (br s, 4H, NH_2). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56%; H, 5.18%. Found: C, 68.44%; H, 5.02%.

Preparation of 3,4-Bis(4-aminophenoxy)benzene−Methanol (3b). A THF (50 mL) solution containing methyl 3,4-bis(4-aminophenoxy)benzoate (2.50 g, 7.14 mmol) was added dropwise to a THF (75 mL) solution/suspension containing LAH (1.50 g, 39.5 mmol). A gentle reflux was maintained during the addition as well as controlling evolution of hydrogen gas. After complete addition of the ester solution, the mixture was heated at reflux for an additional 16 h with stirring. The mixture was carefully quenched with water (1.5 mL), 15% aqueous NaOH (1.5 mL), and water (4.5 mL) and then dried over magnesium sulfate. The solution was filtered and the THF removed under reduced pressure to afford pure **3b** as a colorless oil (2.33 g, 80%). The yield is adjusted for the sample containing ~3 wt % of THF as determined by proton NMR spectroscopy. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 6.90 (dd, J = 8.3 Hz, J = 1.8 Hz, 1H, H2), 6.82 (d, J = 8.3 Hz, 1H, H3), 6.81 (d, J = 1.8 Hz, 1H, H6), 6.71 (d, J = 8.7 Hz, 2H, Ar′H2), 6.69 (d, J = 8.7 Hz, 2H, Ar′H2), 6.56 (d, J = 8.7 Hz, 2H, Ar′H3), 6.55 (d, J = 8.7 Hz, 2H, ArH3), 5.14 (t, J = 5.6 Hz, 1H, −OH), 4.91 (s, 2H, $-NH_2$), 4.87 (s, 2H, $-NH_2$), 4.36 (d, J = 5.6 Hz, 2H, $-CH_2$). ^{13}C NMR (DMSO-d_6) δ: 148.6, 147.3, 146.6, 146.5, 145.0, 144.6, 138.0 (aromatic C's), 120.9, 119.7, 119.0, 116.6, 114.9, 114.8 (aromatic CH's), 62.3 (CH_2). Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.83%; H, 5.63%; N, 8.69%. Found: C, 70.51%; H, 5.44%; N, 8.54%.

Preparation of CH_2OH-Functionalized Polyimide (4). A Schlenk flask was charged with monomer **3a** (5.430 g, 16.14 mmol), 6F-4,4′-diamine (8.094 g, 24.21 mmol), and NMP (70 mL). Once the solution was homogeneous the amine solution was added to a NMP (70 mL) solution 6-FDA (16.853 g, 37.93 mmol) and phthalic anhydride (717 mg, 4.84 mmol, 6 mol % end-cap). The mixture was stirred at ambient temperature for ~16 h and then fitted with a reflux condenser and immersed in an oil bath heated to 180 °C for 6 h. The reaction vessel was removed from the oil bath, allowed to spontaneously cool for 30 min, and then poured into a vigorously stirred solution of methanol (2 L). Vigorous stirring of the methanol was maintained during the entire precipitation process. The precipitated polymer was then collected on a medium-porosity glass frit, washed with methanol (~2 L), and then dried under reduced pressure for 12 h at 80 °C. Polyimide **4** was isolated as an off-white solid (23.65 g, 80%, M_n 6500, polydispersity 2.3, T_g 268 °C). ^{1}H NMR ($CDCl_3$) δ: 7.85−8.10 (m, 17 H), 7.50−7.65 (m, 10 H), 7.38 (br s, 4 H), 7.13 (br s, 4 H), 6.83 (s, 2 H), 6.72 (s, 1 H), 4.63 (s, 2 H). Selected ^{13}C NMR ($CDCl_3$) signals: δ 166.3, 166.2, 165.9, 165.8 (carbonyls), 158.2, 156.9 (aromatic C's), 131.3, 128.2, 126.6, 119.5, 112.7 (aromatic CH's), 64.6 (CH_2OH). Anal. Calcd for **4**: C, 58.37%; H, 2.28%; N, 3.84%. Found: C, 58.22%; H, 2.17%; N, 3.95%.

Preparation of CH_2OH-Functionalized Polyimide (5). In a similar manner as above, a Schlenk flask was charged **3b** (1.55 g, 4.56 mmol), 6F-4,4′-diamine (2.285 g, 6.83 mmol), and NMP (25 mL) and stirred until homogeneous. In one portion was added 6-FDA (4.760 g, 10.72 mmol) and phthalic anhydride (202 mg, 6 mol % end-cap). This mixture was allowed to react with stirring at ambient temperature for 12 h and place in an oil bath maintained at 180 °C for 6 h. The mixture was removed from the oil bath and after ~30 min poured into methanol (~1 L) and isolated as above. This afforded polymer **5** as an off-white powder (6.77 g, 79%, $M_n \sim$ 5300, polydispersity 1.7, T_g 283 °C). ^{1}H NMR ($CDCl_3$) δ: 8.12−7.8 (m, ~16 H), 7.6−7.55 (m, ~11 H), 7.34 (d, J = 8.8 Hz, 4 H), 7.18 (br s, 2 H), 7.01 (d, J = 8.8 Hz, 4 H), 4.62 (s, 2 H). Anal. Calcd for **5**: C, 58.37%; H, 2.28%; N, 3.84%. Found: C, 57.41%; H, 2.27%; N, 3.64%.

Reaction of Polyimide with Hexamethyldiisocyanate (6). A homogeneous THF (10 mL) solution containing **4** (1.00 g, ~0.63 mequiv of $-CH_2OH$) and triethylamine (5 mL) was heated to 55 °C and then treated with 1,6-diisocyanatohexane (~3.0 mL, 18.4 mmol), and the reaction continued at 55 °C for 2 h with stirring. The warm solution was poured into 200 mL of ether to precipitate the polymer. The off-white polymer was collected on a glass frit and washed with additional ether (~200 mL) and then hexanes (~300 mL). The polymer was dried under reduced pressure to afford the functionalized isocyanate polymer **6** (1.00 g, 90%). Selected ^{1}H NMR (DMSO-d_6) data: δ 4.98 (s, 2H, CH_2O), 3.1−2.8 (m, 4 H, CH_2NCO and CH_2NHCO), 1.4−1.0 (m, 8 H, CH_2's). IR (film) $\nu_{N=C=O}$ 2271 cm^{-1}.

Reaction of the Pendent Isocyanate with DR-1 (7). A methylene chloride (20 mL) solution of polymer **6** (1.00 g) was treated with DMAP (203 mg) and stirred for 10 min. DR-1 (0.314 g, 1.00 mmol) was added in one portion, and the resulting dark red solution was allowed to stir overnight with stirring under nitrogen. The solution was poured into MeOH (300 mL) to precipitate the polymer. The polymer was collected on a glass-frit and washed with MeOH (200 mL), ether (150 mL), MeOH (100 mL), and ether (100 mL) and then dried under reduced pressure for 16 h. This afforded polymer **7** (0.96 g, 74%, T_g 199 °C) as a bright red powder. ^{1}H NMR ($CDCl_3$) δ: 8.30 (d, J = 8.5 Hz), 8.10−7.82 (m), 7.70−7.55 (m), 7.41 (d, J = 8.8 Hz), 7.16 (d, J = 8.8 Hz), 6.9−6.70 (m), 5.06 (s, 2 H), 4.77 (br s, NH), 4.25 (m, OCH_2CH_2N), 3.68 (m), 3.50 (m), 3.30−2.90 (m, $-CH_2NH$), 1.7−1.2 (m, CH_2's and CH_3). Anal. Calcd: C, 58.66%; H, 3.12%; N, 6.69%. Found: C, 58.18%; H, 3.27%; N, 6.55%.

General Procedure for the Modification of PI-CH_2OH with a Diacid Chloride. A THF solution (10 mL) containing **4** or **5** (1.00 g, 0.53 mequiv), 2,6-di-*tert*-butylpyridine (200 mg, 0.97 mmol), and DMAP (20 mg, 0.16 mmol) was treated with the appropriate diacid chloride (~7 mmol). Some precipitate forms over the reaction a period of 16 h, and the mixture was allowed to react with stirring for time ranging from 16 to 20 h. The mixture is filtered through a plug of Celite (1 × 2.5 cm) into a rapidly stirred solution of ether (150 mL). The polymer was collected by filtration taking care to protect the solution and polymer from air and then dried under reduced pressure (0.2 Torr) in Schlenk flask for 1 h to afford ~800−900 mg of modified polymer. The material does contain residual ether (~5 wt %) and is used immediately for the next reaction without purification.

Attachment of an Organic Dye to Acid Chloride-Functionalized PI. A typical procedure is as follows: The functionalized polyimide (**8**, **9**, or **10**, 1.00 g, 0.49, 0.49, and 0.43 mequiv, respectively) was dissolved in dichloromethane (25 mL) and then treated with DR-1 (500 mg, 1.59 mmol). This mixture was stirred for ~10 min, and then in one portion DMAP (100 mg, 0.82 mmol) was added. The mixture was allowed to react with stirring for 3 h at ambient temperature. The mixture was added to a rapidly stirred solution of methanol (200 mL), and the polymer was collected on a glass frit (60 mL, medium). The resulting polymer was washed with methanol, ether (50 mL), methanol (100 mL), and ether (50 mL) and then dried under reduced pressure (~0.2 Torr) for 16 h. This typically yielded 1.0 g (85% yield) of polymer with near-quantitative attachment of organic dye as measured by NMR, T_g, and UV−vis spectroscopy. Selected data for the polymers:

Polymer **11** (T_g 168 °C). ^{1}H NMR ($CDCl_3$) δ: 8.30 (d, J = 8.5 Hz, 2 H), 8.10−7.82 (m, ~16 H), 7.65−7.55 (m, ~10 H), 7.41 (d, J = 8.8 Hz, 4 H), 7.16 (d, J = 8.8 Hz, 4 H), 6.9−6.8 (m, 3 H), 6.75 (s, 1 H), 5.06 (s, 2 H), 4.29 (apparent t, 2 H), 3.68 (apparent t, 2 H), 3.53 (m, 2 H), 2.45−2.30 (m, 4 H), 1.7−1.5 (m, 4 H), 1.25 (t, J = 7 Hz, 3H). Anal. Calcd: C, 59.10%; H, 2.93%; N, 5.61%. Found: C, 59.39%; H, 3.04%; N, 6.14%.

Polymer **12** (T_g 175 °C). ^{1}H NMR ($CDCl_3$) δ: 8.31 (d, J = 8.5 Hz, 2 H), 8.12−7.8 (m, ~16 H), 7.6−7.55 (m, ~10 H), 7.34 (d, J = 8.8 Hz, 4 H), 7.18 (br s, 3 H), 7.01 (d, J = 8.8 Hz, 4 H), 6.79 (d, J = 8.5 Hz, 2 H), 5.08 (s, 2 H), 4.29 (t, J = 6 Hz, 2 H), 3.68 (t, J = 6 Hz, 2 H), 3.53 (q, J = 7 Hz, 2 H), 2.40−2.25 (m, 4 H), 1.70−1.55 (m, 4 H), 1.27 (q, J = 7 Hz, 3 H). Anal. Calcd for **12**: C, 59.10%; H, 2.93%; N, 5.61%. Found: C, 58.91%; H, 2.98%; N, 5.92%.

Polymer **13** (T_g 156 °C). ^{1}H NMR ($CDCl_3$) δ: 8.30 (d, J = 8.5 Hz, 2 H), 8.10−7.80 (m, ~16 H), 7.65−7.55 (m, ~10 H), 7.41 (d, J = 8.8 Hz, 4 H), 7.16 (d, J = 8.8 Hz, 4 H), 6.78 (br s, 2 H), 6.75−6.68 (m, 2 H), 5.06 (s, 2 H), 4.29 (t, J = 6 Hz, 2 H), 3.68 (t, J = 6 Hz, 2 H), 3.53 (q, J = 7 Hz, 2 H), 2.40−2.25 (m, 4 H), 1.70−1.40 (m, 4 H), 1.35−1.10 (m, 11 H). Anal. Calcd for **13**: C, 59.75%; H, 3.21%; N, 5.42%. Found: C, 59.89%; H, 3.46%; N, 5.72%.

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References and Notes

(1) Resinger, J. J.; Hillmyer, M. A. *Prog. Polym. Sci.* **2002**, *27*, 971−1005 and references therein.

(2) Guillier, F.; Orain, D.; Bradley, M. *Chem. Rev.* **2000**, *100*, 2091−2157 and references therein. Krchnak, V.; Holladay, M. W. *Chem. Rev.* **2002**, *102*, 61−91 and references therein.

(3) Wang, Y.; Erdogan, B.; Wilson, J. N.; Bunz, U. H. F. *Chem. Commun.* **2003**, *14*, 1624−1625. Wagner, M.; Nuyken, O. *Macromolecules* **2003**, *36*, 6716−6721 and references therein.

(4) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31 and references therein Davey, M. H.; Lee, V. Y.; Wu, L. M.; Moylan, C. R.; Volksen, W.; Knoesen, A.; Miller, R. D.; Marks, T. J. *Chem. Mater.* **2000**, *12*, 1679−1693 and references therein. Gubbelmans, E.; Verbiest, T.; Van Beylen, M.; Persoons, A.; Samyn, C. *Polymer* **2002**, *43*, 1581−1585. Lee, J. Y.; Bang, H. B.; Kang, T. S.; Park, E. J. *Eur. Polym. J.* **2004**, *40*, 1815−1822 and references therein.

(5) For examples of Mitsunobu coupling of dyes to phenol-containing polyimides see: Chen, T. A.; Jen, A. K.-Y.; Cai, Y. M. *J. Am. Chem. Soc.* **1995**, *117*, 7295−7296. Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature (London)* **1997**, *338*, 845. Saadeh, H.; Yu, D.; Wang, L. M.; Yu, L. P. *J. Mater. Chem.* **1999**, *9*, 1865.

(6) For additional examples of chemical modification of polyimide backbones containing phenolic groups see: Ueda, M.; Nakayama, T. *Macromolecules* **1996**, *29*, 6427−6431. Yu, H.-S.; Yamashita, T.; Horie, K. *Macromolecules* **1996**, *29*, 1144−1150. Chen, H.; Yin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1735−1744. For pendent carboxylic acid groups

see: Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. *Macromolecules* **2003**, *36*, 1882−1888.

(7) Luo, J.; Haller, M.; Li, H.; Tang, H. Z.; Jen, A. K.-Y.; Jakka, K.; Chou, C.-H.; Shu, C.-F. *Macromolecules* **2004**, *37*, 248−250 and references therein.

(8) An alternative and less efficient synthetic route to compound **2a** has been reported previously: Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1999**, *32*, 2215−2220.

(9) Guenthner, A. J.; Pentony, J. M.; Lindsay, G. A. In *Linear and Nonlinear Optics of Organic Materials IV*; Norwood, R. A., Eich, M., Kuzyk, M. G., Eds.; *Proc. SPIE*; SPIE: Bellingham, WA, 2004; Vol. 5517, pp 175−186.

(10) Zhang, C.; Dalton, L. R.; Oh, M. C.; Zhang, H.; Steier, W. H. *Chem. Mater.* **2001**, *13*, 3043−3050.

(11) Wu, L. M.; Knudsen, A. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 217.

(12) Banach, M. J.; Clarson, S. J.; Beaucage, G.; Benkoski, J.; Mates, T.; Kramer, E. J.; Vaia, R. A. *J. Appl. Polym. Sci.* **2002**, *86*, 2021.

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