A Generic Approach to Functionalizing Aromatic Polyimides for Second-Order Nonlinear Optics

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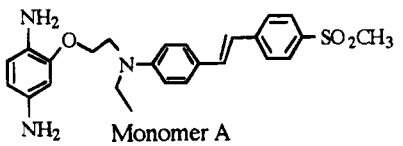
Received September 7, 1994
Revised Manuscript Received November 28, 1994

In our previous work, we successfully synthesized an aromatic polyimide functionalized with a nonlinear optical (NLO) chromophore((dialkylamino)sulfonylstilbene).[1] In that synthetic approach, we utilized the advantage that the sulfonyl group in the NLO chromophore is not sensitive to $SnCl_2$ and prepared the diamino monomer A from the corresponding dinitro compound. Although this approach is applicable to NLO chromophores which are not sensitive to $SnCl_2$, the limitation of the process is obvious. For example, the chromophores bearing nitro groups will not be tolerated and those with an azo linkage will also be reduced. To synthesize polyimides functionalized with NLO chromophores exhibiting larger electro-optic (E-O) coefficients, a generic synthetic approach is needed. Recently, we have developed such an approach, which is shown in Scheme 1. This approach enables us to synthesize different NLO chromophores with the diamino functionality.

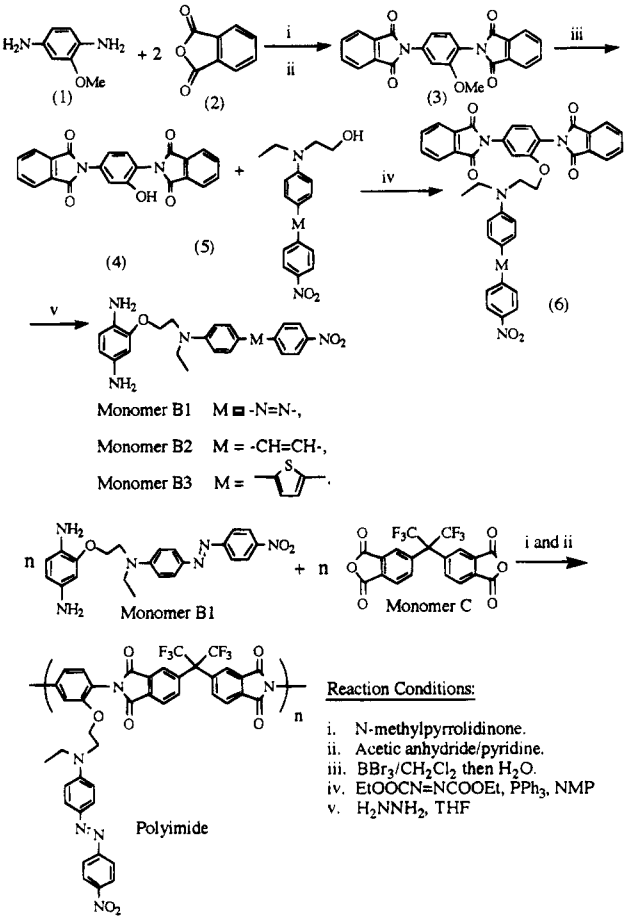


Monomer A

Depending on the applications, the dipole alignments in NLO polymers can be achieved either by corona poling or by parallel-electrode poling. For applications in waveguide devices, however, parallel-electrode poling is favored due to its flexibility in device patterning.[2,3] A problem occurs for poly(amic acid) materials when the poling is effected by the parallel-electrode method. Because the imidization step releases water molecules, they are detrimental to the deposited electrode such as a gold electrode. To solve this problem, ideally, a soluble, functionalized polyimide with a high glass transition temperature should be utilized. Indeed, soluble polyimides without functionality are known in the literature.[4,5] For example, when 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, monomer C in Scheme 1) was used to polymerize with various diamino monomers, soluble polyimides with high T_g were obtained. If our diamino NLO chromophores are utilized to react with this dianhydride monomer, the desired soluble NLO polyimides can be synthesized. We prepared such a polyimide (see Scheme 1), which exhibited an excellent film-forming quality. Preliminary E-O coefficient measurements revealed a large E-O coefficient, 27 pm/V at 780 nm. In this paper, we describe the synthetic approach and report preliminary physical studies on one of the resulting polyimides.

The chemistry involved in the synthesis of this polyimide is shown in Scheme 1. Compound **1** was protected by diimido groups, and the resulting compound **3** underwent ether cleavage with boron tribromide to yield compound **4**. The Mitsunobu reaction between compounds **4** and **5** led to the formation of

Scheme 1. A Generic Approach to Functionalized NLO Polyimides



compound **6**.[1] Because of the poor solubility of compound **4** in THF, DMF, and DMSO, the reaction was carried out in NMP. The hydrazinolysis of compound **6** gave the desired diamino monomer B. Monomer B can be easily purified by recrystallization from methanol. The spectroscopic and microanalytic results supported the structure as expected.[6] Three monomers with different NLO chromophores were synthesized (see Scheme 1). In this paper, we describe the detailed characterization of the polyimide derived from monomer B1.

The polymerization was carried out under nitrogen in NMP at 5 °C for 30 min and the solution was then warmed to room temperature for 1 h. The reaction mixture became very viscous (sometimes, the reaction mixture formed a gel which dissolved in the reaction mixture during the imidization process) and the resulting poly(amic acid) was then imidized chemically using acetic anhydride/pyridine as the cyclizing reagent. The resulting solution was then precipitated into methanol. The solid was recovered and purified by dissolving it in THF and reprecipitating it into methanol. The polymer collected was washed with methanol in a Soxhlet extractor for 2 days and then dried under vacuum at 60 °C for 2 days.

The resulting polyimide was soluble in many organic solvents, such as THF, chloroform, tetrachloroethane, DMF, DMSO, and NMP. Optical-quality films can be prepared either by spin-coating or casting on glass substrates (or ITO glass). The films can be peeled off by dipping them into water, and tough free-standing films can be obtained. Due to the good solubility of the

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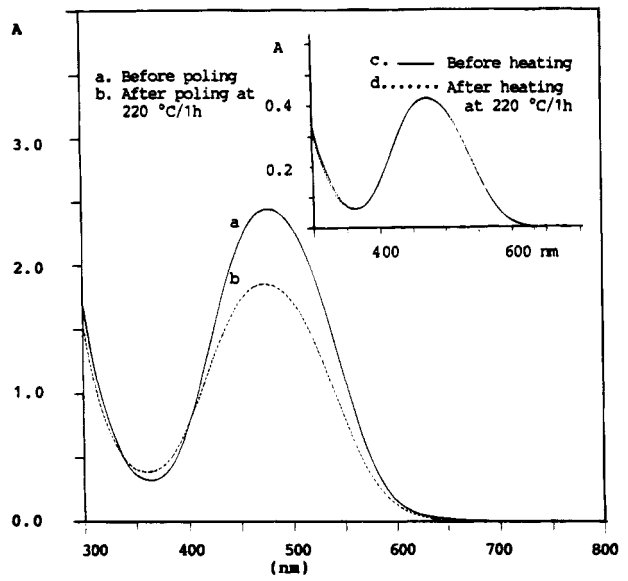

Figure 1. UV/vis spectra of the polyimide: (a) and (b), before and after poling; (c) and (d), before and after thermal treatment.

polyimide in THF, the molecular weight can be measured by using GPC. A weight-averaged molecular weight (M_w) of 35 000 with a polydispersity of 2.5 was obtained (polystyrenes as standards).

The polymer structure was characterized by various spectroscopic studies. No chemical shift due to the amic acid protons was observed in the ^{1}H NMR of the polyimide, indicating that the imidization process was almost complete. The three sets of chemical shifts at 8.19, 7.66, and 6.62 ppm were attributed to the aromatic protons of the chromophore. Another set of aromatic protons of the chromophore overlapped with the aromatic protons of the 6FDA moieties between 7.8 and 8.0 ppm. The chemical shifts of the three protons of the benzene ring bearing the two amino moieties were around 7.34, 7.19, and 7.16 ppm. The chemical shifts of the aliphatic protons appeared at 4.23, 3.71, and 1.06 ppm, similar to that of the diamino monomer.

The FTIR spectrum of the polyimide exhibited the typical absorptions for a polyimide.[1] The absorptions at 1785, 1728, and 722 cm^{-1} are characteristic of an imide ring. Two absorption peaks around 1516 and 1339 cm^{-1} were due to the nitro group on the NLO chromophore.

The thermal characterizations of the polyimide were carried out by using TGA and DSC. A glass transition temperature (T_g) of ca. 238 °C was observed in DSC studies. TGA studies indicated that the polyimide started to decompose at 319 °C (the turning point temperature on the TGA trace, under nitrogen).

The electronic absorption spectra of the polymer were taken using a Cary 2415 spectrophotometer and are shown in Figure 1. They exhibited a typical absorption due to the diazo chromophore with a maximum at 478 nm. To induce the second-order optical nonlinearity, the polyimide was poled under a high electric field of 5.5×10^6 V/cm near its glass transition temperature (220 °C) for 1 h. After poling, the maximum absorption for the NLO chromophore was blue shifted to 475 nm ($\delta\lambda$ = 3 nm) and the absorbance decreased due to the alignment of the chromophore's dipole moment. The order parameter ϕ (=1 − A_2/A_1, where A_1 and A_2 are the UV/visible absorbances before and after poling), which is related to the poling efficiency, was deduced to be 0.24. The corresponding polymer film which was thermally treated without poling at 220 °C for 1 h under nitrogen showed no change in the absorption spectrum. This indicated that the chromophore could survive in that temperature range for a short time. The FTIR spectra also indicated that before and after curing at 220 °C, the magnitudes and the positions of the absorption bands of the nitro group are identical.

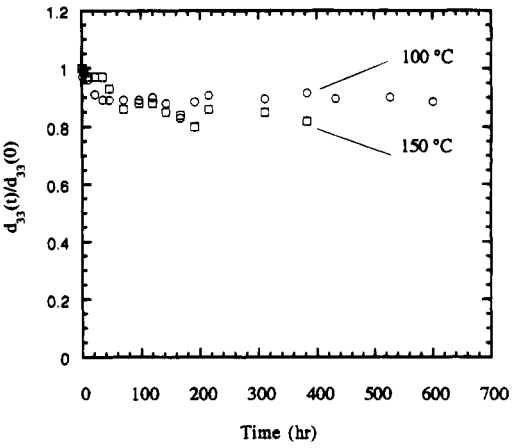

Figure 2. Temporal stability of the SHG signal of the polyimide at (a) 100 and (b) 150 °C.

The refractive indicies of the polyimide were measured by using a Metricon Model 2010 prism coupler at 632 and 780 nm. The refractive indicies at 532 (second harmonic wavelength) and 1064 nm (fundamental wavelength) were deduced from the corresponding Sellmyer relationship and found to be 2.0622 and 1.6128, respectively.

The second harmonic generation (SHG) measurements were performed at a wavelength of 1064 nm using a mode-locked YAG:Nd laser (Continuum-10 with a pulse width of 25 ps and a repetition rate of 10 Hz) as a fundamental light source (1.064 μm).[1,7,8] A large resonant-enhanced d_{33} value of 169 pm/V was observed. From the approximate two-level model, the nonresonant value, $d_{33}(\infty$ nm), was evaluated to be 18 pm/V.[9] This result indicated that the major component in the d_{33}(532 nm) was from the resonant contribution, which is not a desired property. Further work to enhance the nonresonant contribution is in progress.

The temporal stabilities of the second harmonic signal under different temperatures were studied by monitoring the SHG signals as a function of time. The results are shown in Figure 2. The SHG signal exhibited no decay at room temperature. It decayed at the beginning and then maintained at ca. 90% of the initial values after standing in air at 100 °C for more than 600 h. At 150 °C in air, more than 82% of the original signal was retained after 300 h after a similar initial decay. It is very interesting to notice that the stability of this soluble polyimide is not as good as the corresponding aromatic polyimides which are not soluble after being imidized. However, these results are still very promising for practical applications considering the good processibility and the flexibility of parallel-electrode poling for device structures.

Most of the interesting device elements, such as the electro-optic modulator, utilize the electro-optic coefficient, r_{ij}. For this polyimide system, an r_{33} value of 27pm/V at 780 nm was observed by using the reflection measurement scheme developed by Teng and Man.[10] This is a sizable value compared with other high-temperature E-O polymers.[11]

In summary, we developed a generic approach to the synthesis of second-order NLO polyimides. A soluble polyimide bearing Disperse Red 1 was synthesized. This polyimide exhibited good processibility and a high optical nonlinearity. A high thermal stability at 150 °C was also observed. Due to the wide availability of the dianhydride monomers and different NLO chromophores, this approach is clearly versatile. This approach is versatile not only for the synthesis of NLO polyimides but also for the synthesis of other functionalized polyimides and polyamides, such as those with liquid crystal side chains. We are presently exploring these different aspects.

Acknowledgment. This work was supported by the Office of Naval Research (Grant N00014-93-1-0092) and the National Science Foundation (Grant DMR-9308124). Support from the National Science Foundation Young Investigator program and the Arnold and Mabel Beckman Foundation (Beckman Young Investigator Award) is gratefully acknowledged.

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