Electrooptic Properties of Side-Chain Polyimides with Exceptional Thermal Stabilities

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Received December 5, 1994
Revised Manuscript Received February 9, 1995

An electrooptic polymer is one in which the index of refraction can be changed by the application of an external electric field. Such materials can be used as active elements in high-speed light modulators and switches. Because of these potential applications, this class of materials has received much recent attention.[1] In order to be useful, several key properties must be optimized: the polymer's electrooptic response must be sufficiently large, this response must be stable at all temperatures that the polymer will experience in processing and in operation, and the attenuation of light in the polymer by scattering and by absorption must be low. In this paper a class of thermoplastic side-chain polyimides is described which have exceptional thermal stabilities without significant sacrifice of optical nonlinearity.

Electrooptic polymers consist of a dipolar chromophore with a high intrinsic molecular hyperpolarizability β, oriented in a polymer host by electric field poling. It has recently been shown[2] that replacement of aliphatic dialkylamine electron-donating groups with diarylamino groups in nonlinear optical chromophores results in a significant increase in thermal stability with little change in the hyperpolarizability. The next step in the design of thermally stable electrooptic chromophores is to incorporate these stable chromophores into a polymer host. The simplest way of doing this is to dissolve the molecule as a dopant in the polymer. It has been shown that the decay of the electric field poling induced orientation of the chromophore in such a guest–host system depends primarily on the glass transition temperature T_g of the guest–host system.[3] There are several reasons why one might not want to use guest–host electrooptic polymer systems. First, the chromophore is "loose" in the polymer and can volatilize during high-temperature processing. Second, in order to achieve as large an electrooptic coefficient *r* as possible, the chromophore concentration must be as high as possible, frequently in excess of 30 wt %. It is often not possible to dissolve a chromophore into a polymer at such a high concentration without phase separation. Even when it is possible, substantial reduction in the glass transition temperature usually occurs at high chromophore loading with a corresponding decrease in the stability of the electric field poling induced ordering of the chromophores.

The approach that we describe here is to incorporate a thermally stable, nonlinear chromophore into a high-T_g polyimide as a chemically attached side chain. Variants of this approach have been described by others.[4] In our approach, the chromophore is a diamine which can be reacted with a number of dianhydrides to produce a variety of polyimides. This approach has the advantage of permitting one to vary the physical properties (such as T_g, solubility, and optical transparency) of the resulting electrooptic polymer by varying the dianhydride. The electrooptic properties can be optimized by appropriate choice of both the diamine chromophore and the dianhydride.

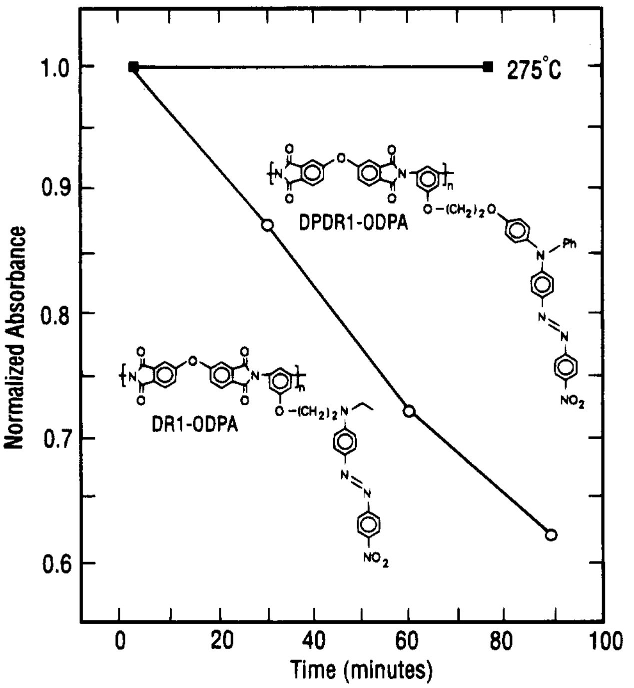
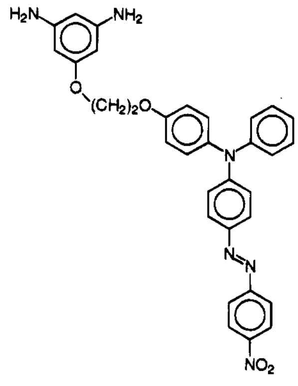


Figure 1. Thermal stability of two side-chain polyimides at 275 °C measured by following the change in absorbance at 484 nm of a thin film of the polymer as a function of time.

To illustrate the approach outlined above, the functionalized diamine **1** was prepared by nucleophilic displacement as described in ref 5. The diamino monomer (mp 106–108 °C) was purified by extensive recrystallization from ethanol. In a similar fashion, the diamine **2** (mp 190–191 °C) could be prepared from the commercially available dye, Disperse Red 1 (DR1). The monomer **2** was recrystallized from acetone/methylcyclohexane. The purity of both **1** and **2** was assured by HPLC analysis using an HP1090 liquid chromatograph (60 × 4.6 mm; 3 μm Hypersil ODS, acetonitrile/aqueous phosphate buffer, gradient elution (0–100%)). Equimolar quantities of either **1** or **2** and purified oxydiphthalic anhydride (ODPA) were mixed in dry *N*-methylpyrrolidinone (NMP) containing 20% *o*-xylene and allowed to react for 15 h at 25 °C. This reaction resulted in the formation of the corresponding poly(amic acids). Since both polyimides (DPDR1-ODPA and DR1-ODPA; see Figure 1) resulting from the chemical imidization with acetic anhydride/pyridine were insoluble in



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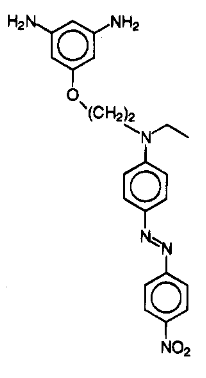

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common organic spinning solvents, polymer films of the soluble poly(amic acids) were spun cast from the reaction solvent (14 wt % solids) at 3500 rpm and then subsequently thermally imidized. The thermal cycle imidization involved heating at 80 °C for 1 h, 150 °C for 1 h, 200 °C for 0.5 h, 250 °C for 0.5 h, and finally 275 °C for 0.5 h. The glass transition temperature of the resulting DPDR1-ODPA polyimide was 227 °C, while that of the DR1-ODPA was 235 °C, as determined by DSC analysis at a heating rate of 20 °C/min. The sample films for the variable-temperature UV–visible studies were cast and cured similarly after dilution with solvent to obtain the proper film thickness upon spinning (0.1–0.3 μm). In this case the spinning time was reduced to ~20 s to minimize adhesion problems.

The thermal properties (thermal gravimetric analysis, TGA) of both polymers have been measured. The 5% weight loss temperature of DPDR1-ODPA measured at 20 °C/min is 375 °C. That for DR1-ODPA is lower by approximately 30 °C. The respective decomposition temperatures measured at the same scan rates are 360 and 320 °C. Thermal data, while useful for predicting the order of stability among a series of polymers or chromophores, are not as useful as variable-temperature UV–visible absorption studies for determining use temperatures for these electrooptic materials.

The thermal stability of the side-chain polyimide DPDR1-ODPA measured by variable-temperature absorption is shown in Figure 1. The absorbance at the first long-wavelength absorption maximum (484 nm) is followed as a function of time while heating in air at 275 °C. The thermal stability of the polyimide containing the diphenylamino electron-donating group (i.e., DPDR1-ODPA) is compared to that of the polyimide (DR1-ODPA) with an alkyl-substituted amine donating group produced from ODPA and 2. The DPDR1-ODPA polyimide shows no evidence of decomposition at this temperature after more than an hour of heating, while the DR1-ODPA polyimide has decayed by almost 30% in this time. The polymer DPDR1-ODPA was even stable briefly at 300 °C, a temperature where DR1-ODPA was not stable at all. This substantial difference in thermal stability is entirely due to the enhanced stabilities of diarylamino-substituted chromophores over their dialkylamino-substituted analogs.[2] Figure 1 also illustrates that tethering the thermally stable chromophores to a polyimide backbone via an alkoxy spacer does not, *a priori*, compromise this enhanced thermal stability.

The electrooptic coefficient of the DPDR1-ODPA polymer was measured using an attenuated total reflection (ATR) technique.[6] The polymer was corona poled at 220 °C with a poling electric field of approximately 230 V/μm. In the ATR technique, a laser beam from a diode laser (1.305 μm) is directed into a prism face, with the NLO polymer film pressed against its base. The angle of incidence of the laser beam on the prism face is varied, and sharp reflectivity dips are observed as a result of the excitation of various waveguide modes in the thin NLO polymer film. By applying a low-frequency (~1 kHz) voltage across the NLO film and measuring the resulting changes in the positions of the waveguide modes, one can obtain the electrooptic tensor components r_{33} and r_{13}. The value of r_{33} measured in this way was found to vary from 8.2 to 10 pm/V depending on where across the NLO layer the measurement was made. This variation in r_{33} was probably due to thickness and electric field variations across the polymer film. A value of $r_{13} = 3 \pm 1$ pm/V was also measured.

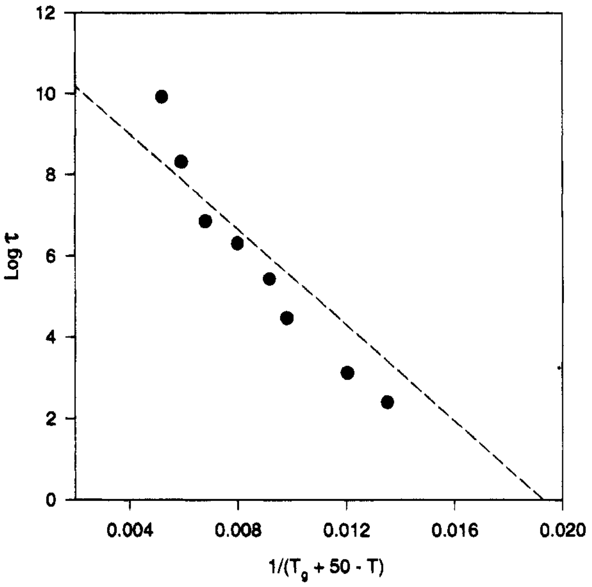

Figure 2. Logarithm of the stretched exponential (eq 1) relaxation time τ as a function of $1/T_g + 50 - T$ for DPDR1-ODPA (solid circles). The dashed line is the line along which a wide variety of guest–host polymer relaxation times lie.[3]

In order to follow the slow decay of the corona poling induced orientational order of the chromophore, the second harmonic signal from a poled DPDR1-ODPA film was measured in the usual way[3] at several temperatures below the polymer glass transition temperature. The observed decay can be fit quite well (but not uniquely) by a stretched exponential functional form[7]

$$\frac{d}{d_0} = \left(\frac{I}{I_0}\right)^{1/2} = \exp[-(t/\tau)^{\beta}] \qquad (1)$$

where d is the second harmonic coefficient and d_0 its value at $t = 0$, I is the intensity of the second harmonic light and I_0 its value at $t = 0$, and t is the time after the poling electric field is removed. The quantity d/d_0 is a measure of the remaining orientational order in the sample and can be shown to be proportional to $\langle\cos^3 \theta\rangle$, where θ is the angle between the molecular dipole moment and the poling axis.[1] One obtains two quantities from the stretched exponential fit, τ and β, that characterize the decay. The quantity τ is useful because it indicates the time it takes the second harmonic coefficient of the system to decay to 1/e of its initial value. In Figure 2, log τ is plotted against $1/(T_g + 50 - T)$. The dashed line in the figure is, for comparison, the empirically determined line along which many guest–host poling relaxation decays have been found to lie.[3] Similar deviations from this "universal" line have been observed for some PMMA side-chain substituted electrooptic polymers.[8] The value of β found for DPDR1-ODPA varies slowly with temperature from a value of 0.3 at 85 °C to 0.6 at 200 °C.

The decay times shown in Figure 2 are obtained by lowering the temperature of the polymer from the poling temperature to the measuring temperature, removing the poling electric field, and beginning measurements immediately. If instead the poling field is held across the sample at the lower temperature for 3.4 h before it is turned off and measurements are begun, the value of τ is found to increase by 50%. Thermal annealing effects of this kind have been observed in other electrooptic polymers.[9]

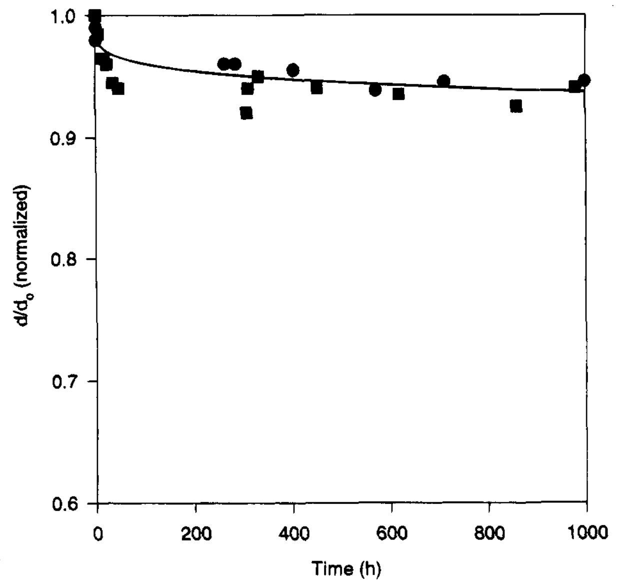

Figure 3. Plot of the normalized second harmonic coefficient as a function time at 85 °C. Solid circles and squares represent relaxation measurements on two different DPDR1-ODPA polymer samples. The solid line is a fit of both sets of data taken together with the stretched exponential function (eq 1).

Figure 3 shows the long time polar order thermal stability of the DPDR1-ODPA polymer of two different film samples at 85 °C. It can be seen that, after an initial small decrease, the second harmonic signal does not significantly change over 1000 h. This observation is consistent with the decay data summarized in Figure 2. From this data one would expect the nonlinearity of the poled polymer system held at 85 °C to decay to 1/e of its initial value only after more than 1000 days! If, after holding the sample at 85 °C for 1000 h, one then raises the temperature of this same sample to 100 °C and maintains the temperature for another 1000 h, no further measurable decay is observed. This is a remarkably good stability for a thermoplastic, non-cross-linked polymer.

In this paper, we have demonstrated a quite general approach to the synthesis of thermally stable electro-optic polymers with high optical nonlinearities. The nonlinearity is optimized by choice of the chromophore from which the diamine monomer is synthesized, while physical properties such as the glass transition temperature and processablity can be optimized by careful choice of the dianhydride portion of the polyimide.

Acknowledgment. This work has benefited greatly from discussions and collaborations with G. Bjorklund, C. Moylan, J. Thackara, and R. Twieg. T.V. is a postdoctoral researcher of the Belgian National Fund for Scientific Research (NFWO). He acknowledges support from the Commission for Educational Exchange between the U.S.A., Belgium, and Luxembourg and from IBM Belgium. This work has been supported in part by the Air Force Office of Scientific Research (Contract No. F49620-92-C-0025), by the Advanced Research Projects Agency (Grant No. MDA972-93-1-0007), and by the National Institute of Standards/ Advanced Technology Program (Cooperative Agreement No. 70NANB2H1246).

Supplementary Material Available: Spectral and analytical data for monomers **1** and **2** (1 page). Ordering information is given on any current masthead page.

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