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Exceptionally Thermally Stable Polyimides for Second-Order Nonlinear Optical Applications

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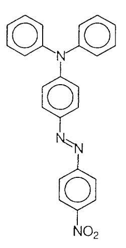
The thermal stability of the electric field induced poled order in a new class of second-order optically nonlinear polymers, "donor-imbedded" side-chain polyimides containing no flexible connectors or tethers to the nonlinear optical (NLO) chromophore, is investigated. In these polymers, the electron-donor part of the chromophore is a diaryl-substituted amine that is incorporated as a part of the polymer backbone. The donor-imbedded systems used in this study have exceptional chemical stabilities at elevated temperatures (350°C) and impressive poled order stability at extremely high temperatures (300°C). In both respects, they were significantly more stable than a true side-chain polyimide with a similar NLO-active chromophore covalently linked to the polymer backbone by a flexible tether group.

Second-order optically nonlinear polymers have potential uses for second-harmonic generation (SHG) (frequency doubling) (*1*) and for very high speed optical switching and modulation (*2*). In order to realize this potential, however, the polymers must withstand temperature excursions during processing that may approach or exceed 300°C and prolonged operation temperatures of up to 100°C. Here we describe a class of exceptionally stable optically nonlinear polyimides some of whose members can be used for periods longer than 1000 hours at temperatures of 225°C and above without any measurable decrease in nonlinearity and that can be held at temperatures greater than 300°C for tens of minutes without thermal degradation or substantial loss in optical nonlinearity.

An electrooptic polymer consists of a dipolar chromophore either dissolved in or chemically attached to a polymer backbone (*3*). The system is made optically nonlinear by raising the polymer-chromophore system above its glass transition temperature T_g in the presence of an electric field. The electric field orients the dipolar chromophores, and after orientation the system is returned to a lower operating temperature before removal of the poling field. In order for the optical nonlinearity, as measured by the electrooptic coefficient *r* (*4*), to be stable during processing and prolonged use, the chromophores must be chemically stable at all temperatures that the system encounters and the orientation of the chromophores must be maintained at these temperatures as well. Recently a class of nonlinear optical (NLO) chromophores containing diarylamino donor substituents with substantial optical nonlinearity and high thermal stability has been described (*5*). Chromophore **1** is such a chromophore. It is a variant of the well-known dye molecule Disperse Red 1 (chromophore **2**) which is stable up to temperatures of 309°C. The substitution of the two phenyl groups for the alkyl groups increases the stability to 393°C. In both cases, the thermal stability is estimated by differential scanning calorimetry (DSC) at a heating rate of 20°C per minute. The value of the decomposition temperature obtained in this way may be high by as much as 60° to 80°C when compared to measurements made by following the chromophore disappearance by monitoring changes in the ultraviolet (UV) absorption spectrum after heating (*6*). The DSC measurements have, however, proved to be a quick way of obtaining the relative ordering. The greatly enhanced stability of the diphenylamino-substituted chromophores over their dialkylaminophenyl-substituted analogs is a surprising, but apparently quite general, phenomenon (*5*). The stability of the electric field–poled ordering can be improved by incorporating these chemically stable chromophores into polymers such as polyimides that have very high T_g's (*7*).



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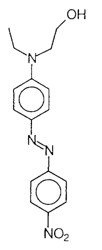

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Incorporation of NLO chromophores into polymers can be accomplished in several ways: by dissolution in a polymer host (a guest-host system); by covalent bonding of the chromophore to the polymer by a flexible tether group (a side-chain system); or by incorporation of the chromophore into the polymer backbone (a main-chain or imbedded side-chain system). Each of these systems has its own set of advantages and disadvantages, but it is generally believed that covalently bonded polymers, either side chain or main chain, will ultimately be necessary for use in practical devices.

We report the exceptional thermal stability of the electric field–induced (poled) order in a class of polyimides in which the electron donor group of the chromophore is incorporated directly into the backbone of

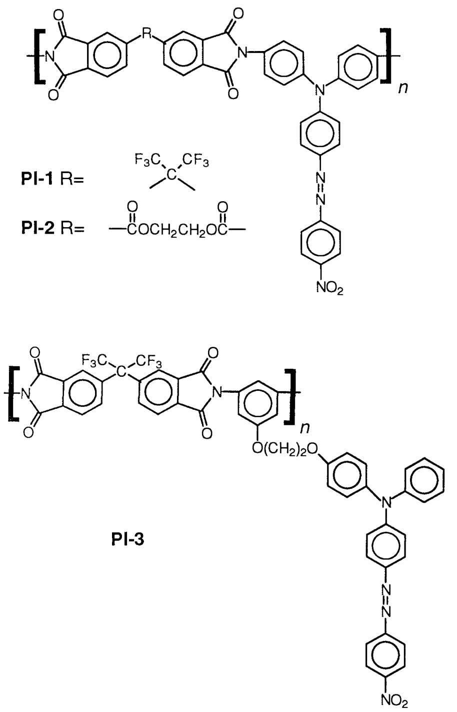

Fig. 1. Chemical structures of **PI-1**, **PI-2**, and **PI-3**.

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the polymer without any flexible connector functionality. The thermally stable donor-imbedded side-chain polyimides were prepared by the condensation of a dianhydride with an NLO diamine to form first a polyamic acid and subsequently the polyimide. The diamine contains the diphenylamino-substituted nitrobenzene chromophore. In principle, different diamine chromophores could be used to enhance the optical nonlinearity and to optimize other physical properties. The dianhydride can be varied to modify polymer properties such as T_g, solubility, and adhesion. Donor-imbedded polyimides that incorporated less stable dialkylamino-substituted chromophores with flexible connector groups have been previously reported (*8*).

Two dianhydrides are used in the current study, either hexafluoroisopropylidene diphthalic anhydride (6FDA) or the ethylene glycol ester of trimellitic anhydride (TMEG). The diamine used to produce the main-chain polymers is *N*,*N*-(bis(*p*-aminophenyl)amino)azo-4′-nitrobenzene. Diamine and dianhydride were reacted to form the polyamic acid, and then chemical imidization with acetic anhydride-pyridine produced the polyimide. A more detailed description of the synthesis is given in (*9*). When 6FDA was used, the polyimide **PI-1** in Fig. 1 was formed, and when TMEG was used, **PI-2** was formed. The chromophore percentage by weight in the polymers was 53% for **PI-1** and 58% for **PI-2**. For comparison, a side-chain polyimide **PI-3** prepared as described in (*10*) contains a similar NLO-active chromophore (45 weight %) that is covalently linked to the backbone by a flexible aryloxyalkyl tether group. All of the systems contain chromophores with diarylamino donor substitution.

The T_g values of all three polyimides shown in Fig. 1 were determined by dynamic mechanical thermal analysis or DSC (heating rate 20°C per minute) or both. The values obtained were 350°C for **PI-1**, 252°C for **PI-2**, and 228°C for **PI-3**. The value measured for **PI-1** is greater by more than 100°C than corresponding values reported for other NLO polyimides. Variable-temperature UV-visible absorption studies indicated that **PI-1** was stable toward chemical degradation at 350°C for several hours, whereas **PI-2** and **PI-3** were stable to 300° and 275°C, respectively. **PI-1** was even relatively stable (<15% decomposition) at 380°C for 20 min. All of the polymers were soluble in the imidized form, and good optical quality films (losses in unpoled films of ≈2 dB/cm at 1305 nm) could be obtained by spin coating onto indium tin oxide (ITO)–coated quartz substrates from a suitable solvent (**PI-1** in cyclopentanone and **PI-2** and **PI-3** in 1,1,2,2-tetrachloroethane). After spinning, all of the polymer samples were heated in an oven at 225°C for several hours to remove residual solvent.

The polyimides were electric field–poled for ~45 min by using either a corona discharge (*11*) or by contact poling between two conducting electrodes. The poling temperatures were 310°C for **PI-1**, 265°C for **PI-2**, and 225°C for **PI-3**. For the electrode poling experiments, a small gold top electrode was evaporated on the polymer-coated ITO-quartz substrates. The relevant electrooptic coefficient r_{33} of electrode poled samples was measured by an ellipsometric technique described by Teng and Man with a diode laser at 1305 nm (*12*). The poling progress was monitored by following the second harmonic light (523.5 nm) generated in the polymer samples. A pulsed 1047-nm Nd:YLF laser was used as the excitation source.

Relaxation of the poled NLO chromophores at different temperatures was followed by monitoring the decrease of the SHG signal emanating from the samples as a result of the decay in the poled order (*13*). The observed decay can be fit quite well by a stretched exponential function (*14*):

$$[I(t)/I(0)]^{1/2} = \exp[-(t/\tau)^{\beta}] \qquad (1)$$

where $I(t)$ is the intensity of the second harmonic light at time t after the removal of the poling electric field, the quantity $[I(t)/I(0)]^{1/2}$ is a measure of the degree of orientational order in the sample and is proportional to the electrooptic coefficient r, τ is the time that it takes the system to decay to $1/e$ of its initial value $I(0)$, and β may vary between 0 and 1 and describes the breadth of the distribution in relaxation times. When $\beta = 1$ the decay is exponential; for $\beta < 1$ the time taken to decay the second $1/e$ is longer than τ. Equation 1 is considered here simply as a way to describe the normalized decay with only two adjustable parameters. Other functional forms can also be used to describe the decay, and the physically correct form to use is still a matter of discussion (*15*).

The measured values of r_{33} depend on the strength of the electric field used to pole the system. For **PI-1** and **PI-2**, the values per unit poling field at 1305 nm obtained by either electrode or corona poling are 0.029 ± 0.007 (pm/V)/(V/μm) and 0.033 ± 0.0035 (pm/V)/(V/μm), respectively. These values, when compared to an electrooptic coefficient of 0.040 ± 0.008 (pm/V)/(V/μm) for the side-chain polymer **PI-3**, show that there is no significant difference between the imbedded-head and side-chain system and are consistent with the roughly similar chromophore density in all three polymers. These systems yield experimentally measured r_{33} values at 1305 nm of 4 to 7 pm/V when poled in an electric field of 160 to 180 V/μm.

The observed polar order stabilities are quite different for the donor-imbedded side-chain and side-chain polyimides. Figure 2 shows the experimentally determined relaxation times τ obtained by fitting the SHG decay to Eq. 1 at various temperatures for the three polymers. Values of β were slightly dependent on temperature and increased with temperature from about 0.2 to 0.4. Obviously, the donor-embedded polyimides (**PI-1** and **PI-2**) are significantly more stable at high temperatures as indicated by their much longer relaxation times at any given temperature. The impressive poled order stability observed for **PI-1** is undoubtedly due in part to its very high T_g. The T_g of the conformationally more flexible **PI-2**, on the other hand, while high, is more similar to that of the side-chain polyimide **PI-3** (252° versus 228°C). The increased orientational stability of **PI-2** over **PI-3**

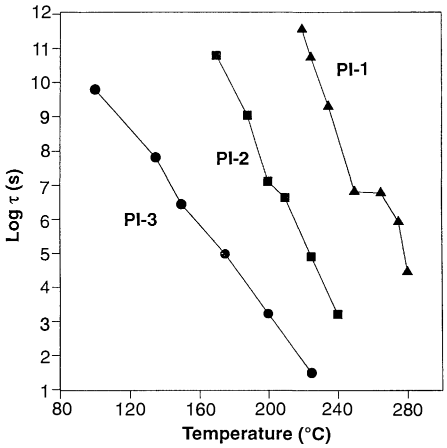

Fig. 2. The relaxation time τ (the point at which the electrooptic coefficient has decayed to 1/*e* of its initial value) as a function of temperature for **PI-1**, **PI-2**, and **PI-3**.

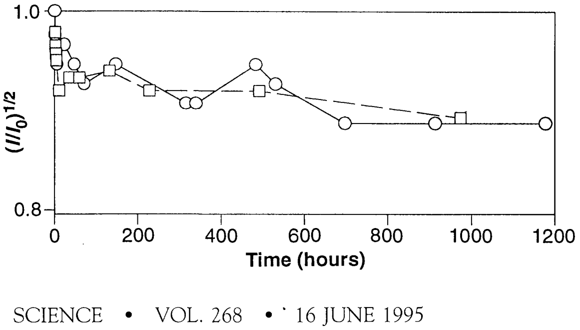

Fig. 3. The decay of the square root of the SHG intensity (proportional to the decay of the electrooptic coefficient *r*) as a function of time. The open circles are for **PI-1** held at a constant temperature of 225°C and the open squares for **PI-2** held at 170°C.

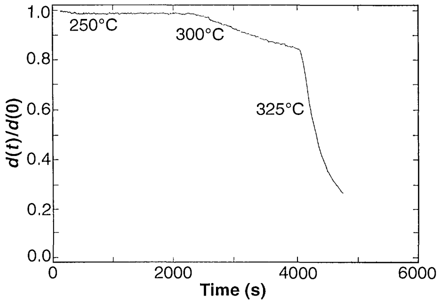

Fig. 4. Decay of the normalized SHG coefficient $d(t)/d(0) = [I(t)/I(0)]^{1/2}$ as a function of time for **PI-1**. This experiment was done on the same sample studied in Fig. 3 after the 1000-hour decay experiment shown in that experiment was completed.

probably results from the stronger coupling of the orientational motion of the NLO-chromophore in both **PI-1** and **PI-2** to the polymer backbone than occurs for the side-chain system **PI-3**. Rearrangement of the chromophores in **PI-1** and **PI-2** thus requires correlated motion of a substantial region of the polyimide backbone.

A poled **PI-1** sample was maintained at 225°C for 1000 hours while monitoring the orientational decay (Fig. 3). After a decrease of ~7% during the first 10 hours, no further measurable change occurred over a period of 1000 hours. Similar long-term stability, also shown in Fig. 3, was observed for **PI-2** held at 170°C. For the side-chain system containing a flexible tether group (**PI-3**), this kind of orientational stability was only observed for temperatures up to 100°C. Figure 4 shows the impressive short-term stability of **PI-1**. Here the polyimide is ramped up in temperature every 2000 s. At 300°C, the polymer loses only ~15% of its nonlinearity over this time increment, which is typical of device processing times.

This class of polymers can meet the severe operating and processing temperature requirements for application of these polymers in integrated optoelectronic devices. With recent advances in identifying chromophores with large optical nonlinearities (*16*) and in improving chromophore thermal stability (*5*), it should now be possible to produce thermally stable NLO polymer systems with large electrooptic coefficients.

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Plant Growth-Rate Dependence of Detrital Carbon Storage in Ecosystems

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Detrital carbon accumulation accounts for most of an ecosystem's capacity to store organic carbon because the carbon contained as plant detritus exceeds that stored in living plants by about threefold. A comparative analysis of the mass and turnover of detrital carbon in ecosystems demonstrates that these properties are strongly related to the turnover rate of the dominant primary producers and are poorly related to ecosystem primary production. These results contribute to an understanding of the factors that control carbon storage in ecosystems and the role of carbon storage in the global carbon budget.

The assessment of factors that control C storage in ecosystems (*1–3*) is essential for determining the role of vegetation in the global C budget (*4*, *5*). Carbon storage in ecosystems is accounted for mostly by the detrital C mass, which amounts to about threefold that accounted for in living plant tissues (*3*, *4*). Hence, knowledge of the factors that control the size and turnover of the detrital C pool in ecosystems should help elucidate the processes that control C sinks in the global C budget (*5*).

In this report we use a broad-scale comparison from published values to show that even though detrital C flux is strongly controlled by ecosystem primary production, neither one is strongly related to the mass and turnover of the detrital C pool. We then demonstrate that plant turnover rate explains a major fraction of the variance in detrital C mass and turnover among ecosystems. We compiled data from reports on aboveground biomass and primary production and the mass and production of detrital C (*6*) from a broad range of ecosystems (*7–11*).

Carbon flux into the detrital pool was strongly and linearly related to primary production (Fig. 1). This linear relation applied both to individual ecosystem types and to all the types grouped together (*12*). On average ~56% of primary production enters the detrital pool, and, with the exception of grasslands, more productive ecosystems yield a correspondingly higher C flow into the detrital pool. Our results support the general findings that litterfall rates are higher in more productive forests (*13*) and that phytoplanktonic primary production is positively correlated to phytoplankton sedimentation rates (*14*).

Detrital C mass was poorly related to both primary production and C flux into the detrital pool (Fig. 2), both of them explaining only ~10% of the variation in detrital C mass among ecosystems. The C mass of the detrital pool varied by about three orders of magnitude for similar values of C flux into this pool (Fig. 2B). The differences in detrital C mass among ecosystems were instead strongly correlated to the plant turnover rate (Fig. 3A); the tendency toward reduced detrital C mass with increasing plant growth rate accounted for 53% of the variance in detrital C mass.

The observations that detrital C mass is relatively independent of C flux into the detrital pool (Fig. 2B), whereas it declines as plant growth rate increases (Fig. 3A) imply that the loss rate of detrital C

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