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We have developed a thermal protocol for the evaluation of NLO chromophores for very high temperature electro-optical applications with poled polymers. This protocol has been demonstrated to have significant predictive utility for EO applications. We have demonstrated that while chromophore thermal instability and nonlinearity are linked, this relationship is not inviolable. Certain thermally stable NLO chromophores have been incorporated into polyimide derivatives either by flexible tether connections or by direct embedding of the donor portion into the polymer main chain. In each case, orientational stabilities for over 1000 hours at 100°C were achieved, so long as the Tg of the polymer exceeded 200°C. The embedding of the chromophore into the main chain gave polymers with exceptional thermal and oxidative stability and polymer Tg values which ranged from 250 − 350°C. Orientational stability of the embedded donor, poled polymers was outstanding and exceeded any reported in the literature, including those examples which had been stabilized by extensive crosslinking. Preliminary results on the low temperature poling of high Tg azo containing polymers by irradiation with polarized light in the presence of an electric field were encouraging as an alternative to thermal poling.

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# FINAL REPORT

## Title: High Temperature Non-Linear Optical Chromophores and Polymers

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## EXECUTIVE SUMMARY

The objective of this contract was the development of thermally stable nonlinear optical chromophores and polymers for use as integrated, on-chip modulators and switches. Such applications require thermal stability of the chromophore as well as thermal and orientational stability of the poled polymer for brief periods in excess of 250° C, temperatures which are associated with polymer poling and device integration. In addition, the orientational stability must be maintained at 80-100° C over the operating lifetime of the device.

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When this project was initiated, there was no accepted technique for estimating the thermal stability of NLO chromophores and their potential for polymeric electro-optic (EO) applications. We have since developed a successful protocol for screening chromophore candidates and have demonstrated its efficacy for polymeric EO applications. In the course of this study, we have prepared a number of new chromophores with good thermal stabilities together with uncompromised molecular nonlinearities. In this regard, the nature of electron donor substituents was found to be the key.

A number of thermally stable NLO chromophores have been incorporated into polyimides either by attachment via a flexible tether or by embedding a functionalized donor substituent into the polymer main chain. NLO polyimides containing tethered substituents show excellent long term orientational stability at moderate temperatures (80-100° C.) From these studies, we have demonstrated that extensive crosslinking is not necessary for the immobilization of poled NLO chromophores so long as the polymer glass temperature exceeds 200° C. However, the Tg values of thermoplastic polyimides with tethered substituents appear to be limited to 250° C or lower. While this is adequate for orientational stability at projected device operating temperatures, it is not acceptable for integration.

The increased rigidity intrinsic to the embedded systems allows Tg values ranging from 250-350° C to be achieved for NLO polyimides. We have actually prepared a polymer of this type containing an azo substituted chromophore with a Tg of 350° C, which is thermally and oxidatively stable to at least 375° C. These numbers begin to approach those achieved for classical high temperature dielectric polymers. Careful high temperature electric field poling of embedded donor NLO polyimides results in measured values of electro-optic coefficients which range from 4-6 pm/V at 1300 nm. The orientational stability of the highest Tg material is truly exceptional and is little changed after more than 1000 h at 250° C. Shorter term orientational stability (~ 30 minutes) was apparent, even at 300° C. This orientational stability far exceeds that of any reported in literature, even for systems which have been extensively crosslinked.

Although electric field poling at very high temperatures (> 250° C) is fraught with many difficulties, we have demonstrated that it is possible, at least in certain cases. However, our recent preliminary results on photoassisted electric field poling (PEP) of high Tg, azo containing polymers at room temperature using polarized light also looks very encouraging and offers a possible alternative to electric field poling at high temperatures for certain structural types.

In summary, we have demonstrated that the thermal stability-nonlinearity trade off for NLO chromophores is not inviolable. For thermoplastic NLO polyimides, the orientational stability in poled systems is closely coupled to the polymer Tg, which in turn depends on the mode of chromophore attachment. As a result, we have prepared NLO polymers with extraordinary thermal and oxidative stability and exceptional orientational stability at elevated temperatures.

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# FINAL TECHNICAL REPORT

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# HIGH TEMPERATURE NLO CHROMOPHORES AND POLYMERS

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## INTRODUCTION

Organic nonlinear optical materials have attracted attention recently as potentially fast and efficient components of optical communication and computing systems. Although they have been studied in many forms including crystals, clathrates, organic glasses, sol-gel composites, vapor deposited films, Langmuir-Blodgett structures, etc., poled polymer films provide the best opportunity for near-term applications, particularly in the area of electro-optic modulators and switches.[1] In this regard, there are two possible scenarios: (i) external applications separate from the silicon device circuitry and (ii) fully integrated electro-optic modulators and switches. Each of these configurations, while sharing certain common characteristics, differ significantly in the thermal stability requirements. For purposes of discussion, we have designated the applications as type I and type II respectively. For each application, long term stability of the polymers (chemical, oxidative and orientational) will be required at operating temperatures which may vary between 80-125°C depending on the configuration and application. Orientational stability in poled samples will require either extensive crosslinking and/or polymers with high glass transition temperatures.[1,2] Regarding the latter, Prêtre et al.[3] have suggested that polymer glass temperatures (Tg) in excess of 170°C will be required to maintain acceptable orientational stability for operation at 100°C over a period of several years. While in situ polymer and/or chromophore crosslinking has been demonstrated to greatly enhance the orientational stability in poled polymer systems,[1,2] there is a price to be paid in terms of reproducibility and manufacturability.

In type II integrated electro-optic applications, the thermal stability requirements are more demanding. The polymer and chromophore must not only survive the poling and elevated operating temperature conditions, but must also be compatible with current semiconductor processing procedures. This may involve brief temperature excursions in the 250-350°C range associated with integration, hermetic sealing, chip connection, etc.[4] Since applications of this type will certainly require wave guide configurations, the losses of the NLO polymer should also be as low as possible and not increase substantially upon poling or processing. A real question for fully integrated electro-optical devices is whether integration and poling of the active polymeric devices can be accomplished without adversely effecting the electrical properties of the operating semiconductor devices. Some progress in this important area has recently been reported by Steier et al.[5]

While much effort has been devoted to the stabilization of polar order in polymer systems, the search for thermally stable NLO chromophores is a much more recent phenomenon.[1,2] Indeed, even the definition of thermal stability for chromophore candidates and comparative assessment is nontrivial. Accordingly, we have developed a protocol useful for screening prospective candidates for high temperature NLO applications and have demonstrated its utility for a number of examples.[6] The procedure involves (i) preliminary screening of candidates by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), (ii) variable temperature UV-visible studies of the chromophores contained as a guest in a soluble polyimide host, (iii) the study by electric field induced second harmonic generation (EFISH) of the effects of heating on chromophore nonlinearity, (iv) solution UV-visible studies on chromophores which have been heated to high temperatures, and finally (v) incorporation of promising candidates into polyimide polymers and studying the thermal and oxidative stability of the bonded chromophore by variable temperature UV-visible spectroscopy. Recently, Professor I. Goldfarb has refined the DSC technique for studying the thermal stability of NLO chromophores using sealed microcapillary techniques.[7] He has calculated the temperature at which 10% of the initial melting point endotherm or the decomposition exotherm is lost for over 30 samples, including some of ours. Our results agree reasonably well with theirs obtained from the decomposition exotherms (vida infra), supporting the validity of our thermal protocol.

## THERMAL STABILITY OF NLO CHROMOPHORES

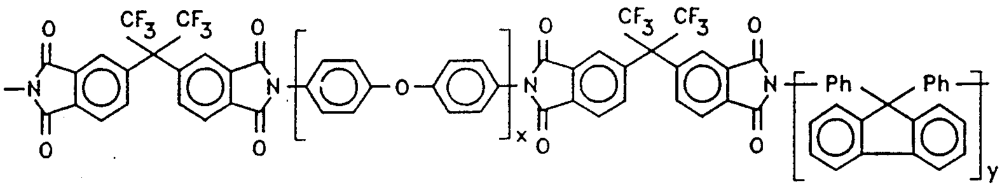
### Thermal Analysis

The simplest and most generally applicable technique for rapidly screening large numbers of candidates is the study of the neat chromophores by thermal gravimetric analysis (TGA) and by differential scanning calorimetry (DSC). From these measurements, we define here a number of thermal events of some utility. In the case of simple TGA analysis, which records the change in sample weight as a function of temperature, we define a quantity $T_5$ as that temperature at which 5% of the original sample weight is lost via volatilization at a heating rate of 20°/minute. This weight loss may represent both volatilization of unaltered sample and/or thermal decomposition and loss of volatile products. The rapid heating rate is essential if the technique is to be useful for the comparative study of large numbers of materials. The use of the TGA technique alone is limited by volatility issues and by the fact that, in principle, not all thermal processes that can effect chromophore nonlinearity are associated with the generation of volatile fragments. In addition, sample volatility alone, while clearly a critical feature for host-guest composites, may not be an issue if the chromophore is chemically bound to the polymer.

DSC analysis, which detects small changes in the heat capacity of the sample, is responsive to thermal events such as melting, sample glass transitions, exothermic or endothermic decomposition, etc. Again, a rapid heating rate of 20°/minute was selected for preliminary scanning of a large number of samples, and materials were sealed in an aluminum pan with a very small hole to reduce volatilization. Ideally, volatile samples should be studied either in sealed tubes or under an increased pressure of inert gas. For our purposes, we have defined a number of pertinent thermal events associated with the DSC analyses. The first is the temperature of the endothermic transition associated with sample melting ($T_m$). High temperature processes associated with decomposition are described by an onset decomposition temperature ($T_d$), defined as that temperature corresponding to the intersection of the tangent of an exothermic (or endothermic) decomposition transition with the adjusted baseline, while $T_{dm}$ is the temperature at the peak of the decomposition. The term $T_d$, where it appears in this paper, refers to data obtained at a heating rate of 20°/minute, unless otherwise noted. Figure 1 shows overlaid TGA and DSC curves for the common azo dye (Disperse Red 1, **1**). Each curve was recorded at a scanning rate of 20° /minute and the pertinent thermal events are marked. The calculated quantity $[(T_d - T_m)]$ can also be an important characteristic, since chromophores that are stable only in the crystalline state (e.g., when $(T_d - T_m)$ is very small) are not likely to be useful for high-temperature poled-polymer applications where the chromophore is diluted by polymer. Pertinent thermal data for a variety of representative NLO chromophores are listed in Table 1. The calculated decomposition onset temperatures ($T_d$)for many of the chromophores listed in Table 1 are above 300°C, which would, at first glance, suggest potential for high temperature applications. However, a number of important caveats apply! First, these data were obtained on neat samples, in an environment which is probably quite different from that experienced in an actual NLO polymer. While one might anticipate that neat samples would provide a "worst case" scenario, particularly where intermolecular decomposition reactions are operative, this is *not* always the case. A second and most important caveat is that the measured decomposition onset temperatures depend strongly on the heating rate. This effect is dramatically demonstrated in Figure 2 for the dye DR1. Slower heating rates lead to markedly lower values for the decomposition onset temperature. The actual variation with heating rate is typically relatively linear for heating rates below 10°/minute. Extrapolation of the linear portion of the plots of onset decomposition temperature vs. heating rate to zero heating rate yields a quantity which we define as the equilibrium decomposition temperature ($T_d^\circ$). In the case of DR1, $T_d^\circ$ =255°C, while the value of $T_d$ measured at 20°/minute is 309°C; a difference of 54°C. As we will see later, the extrapolated value corresponds more closely to a reasonable use temperature for DR1 in high-temperature poled-polymer applications. A number of additional $T_d^\circ$ values are also included in Table I for comparison. In spite of the fact that $T_d^\circ$ values for NLO chromophores represent a more realistic estimate of thermal stability, the extrapolation procedure is still somewhat time consuming and is therefore not readily applicable for broad-based material surveys. Hence, we continue to routinely report $T_d$ values obtained at 20°/minute, a technique which is useful for relative ordering purposes. In many cases, these decomposition onset temperatures have been empirically determined to be as much as 60–85°C[8] *above* reasonable use temperatures for high temperature polymer applications (see below). Furthermore, the exclusive dependence on the thermal analytical techniques described here become less useful, or even inapplicable, for those chromophores whose sample decomposition exotherms (endotherms) are very broad, poorly defined or absent.

### Variable Temperature UV-Visible Spectroscopy

In an effort to better mimic the polymer environment anticipated in poled polymer applications, we have studied the variable temperature UV-visible behavior of NLO chromophores incorporated as guests in a soluble high-temperature polyimide host. For this we have selected the copolymers PI-1 as host materials where the composition was altered by varying the ratio of oxydianiline (ODA) to 9,9′-bis(p-aminophenyl)fluorene (FDA). These polymers are readily soluble in the imidized form in a variety of common organic solvents, most preferably 1,1,2,2-tetrachlorethane. The undoped copolymer glass transition temperatures (Tg) depend on the composition, and range from 300–375°C ($y = 0.25 - 1.0$). In the structure PI-1, the molar ratio of the diamine component(s) ($x + y$) to anhydride is one. The maximum Tg value corresponds to that of the simple copolymer ODPA-FDA (PI-1, $x = 0$), and this is the host polymer most often employed for our variable-temperature UV-visible studies. This material forms high-quality optical films, and most chromophores are readily soluble in the polymer. The NLO chromophores are dissolved at a 5–10 wt.% level based on the dry weight of the polymer. The actual concentration of the chromophore used depends somewhat on its extinction coefficient at the long wavelength ($\lambda_{max}$). Target goals for these studies were thin film optical densities for the long wavelength absorption ranging from 0.5–1.5 (1–2 $\mu$m thick films) to permit accurate measurements using a diode-array, UV-visible spectrometer. With such a machine, the measurement of $\lambda_{max}$ is accurate to ± 2 nm.



PI−1

Variable temperature UV-visible studies on two typical NLO chromophores, DR1 **(1)** and the common laser dye (DCM, **6**), are shown in Figure 3. In each case, the absorbance at the original $\lambda_{max}$ decreases steadily upon heating at 250°C, a temperature still considerably below their respective measured onset decomposition temperatures ($T_d$) as estimated by DSC analysis (see Table I).

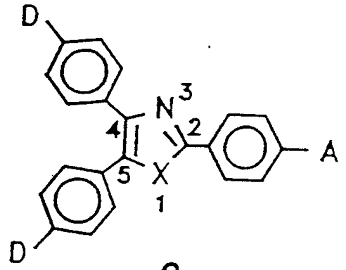
One obvious problem with this particular technique is that the thin film absorbance responds not only to chromophore decomposition, but also to the volatility of the chromophore. The latter depends both on the chemical nature of the chromophore as well as its molecular weight. It is sometimes difficult to clearly distinguish between volatility and decomposition in the absence of a significant thermally-induced change in position of the absorption maximum. However, for many chromophores, the relative importance of volatilization versus decomposition can be qualitatively assessed by consideration of the UV-visible spectra in comparison with the results from TGA analysis. For example, although there is virtually no change in the $\lambda_{max}$ for DR1 in the polyimide host upon heating (Figure 3a), there is an isobestic point around 400 nm and a slight increase in absorbance in the 360 –390 nm region as the absorbance at $\lambda_{max}$ decreases. TGA analysis (20°/minute) of DR1 suggests that some initial weight loss begins around 250°C, which continues until ~80 –85% of the original sample weight is eventually lost by the time the temperature reaches 400°C (see Figure 1). The TGA results suggest that, while a large portion of the sample is lost through volatilization, some decomposition occurs concurrently. A similar conclusion can be reached by examining the overlaid UV-visible spectra in Figure 3a. The situation for the laser dye DCM depicted in Figure 3b is somewhat less ambiguous. Prolonged heating of the composite sample at 250°C causes not only a pronounced drop in the absorbance at the original $\lambda_{max}$ (474 nm), but also a blue-shift and broadening of the long wavelength transition. These data would suggest that significant decomposition of the chromophore is occurring upon heating, even at 250°C. Consistently, TGA analysis of this material shows that although initial weight loss begins at ~250°C, only 30% of the initial sample weight is lost upon continuing the scan to ~400°C.

In general, the interpretation of variable temperature, UV-visible host-guest studies of lower molecular weight NLO chromophores is often complicated by volatilization. For those materials listed in Table I, absorbance losses ranging from 15 –55% were observed upon heating at 250°C for 1h. For most of these materials, volatilization is an important contributor. Studies of these type on chromophore-polymer composites are more informative for higher molecular weight and hence intrinsically less volatile chromophores (vide infra).

## High Temperature NLO Chromophores

### *Azole Derivatives*

The thermal inadequacies of the traditional donor chromophore acceptor substituted stilbenes, tolanes and azo derivatives shown in Table I led us to consider materials containing basic structural elements which are present in many high temperature polymers. For this study, we selected triaryl substituted azoles as illustrated by **9**.[10] Calculations and experiments suggest that the particular substitution pattern shown in **9** exhibits enhanced nonlinearities relative to triarylazoles with donor substituents in position 2 and acceptors in positions 4 and 5.



**9**

Many of the azole derivatives studied had relatively high onset decomposition temperatures ($T_d$), particularly those derivatives containing moderate electron donating substituents. For the imidazole derivative **9a** (D = OMe, A = $NO_2$, X = NH), the improved thermal stability is also reflected by guest-host, variable temperature UV-visible studies. In this case, there was less than 15% loss in the absorbance at the $\lambda_{max}$ (424 nm) after 1h at 300°C, a considerable improvement over any of the materials described in Table I. However, the use of only moderate electron donating substituents also adversely effects the molecular hyperpolarizability. In the case of 2,4,5-triaryl substituted azole chromophores, like many NLO chromophores, the thermal stability and molecular hyperpolarizability seem to be strongly and inversely coupled.[10]

## Thermally Stable Donor-Acceptor Substituted Stilbenes and Azo Derivatives

While this unfortunate relationship is widespread for many chromophores, it is not inviolable. Recently we[8,11-14] as well as others[15-17] have reported the preparation of a variety of thermally stable chromophores with large nonlinearities. Such a favorable situation may be realized even for simple donor-acceptor substituted stilbenes, tolanes and azo derivatives[8,11-14] with appropriate substitution. For amino donor substituents, the thermal stability of the chromophore depends critically on the nature of the substituents attached to nitrogen. This effect was first discovered during DSC studies of a number of readily available azo dyes (see Figure 4). In the case of the 4'-amino-4-nitroazobenzene derivatives, it is clear that the sequential replacement of the hydrogens of the amino group with aryl substituents results in a progressive increase in the thermal stability of the chromophore. This is not the case for substitution with simple alkyl substituents, in fact the opposite is often observed. This result is further demonstrated for a variety of nitro-substituted azobenzene derivatives by the thermal data shown in Table II. In each case, aryl substitution improves the thermal stability, as determined by DSC analysis, and N,N-diaryl substitution leads to the greatest improvement. Nor is the effect limited to azo derivatives; similar improvements in thermal stability are also observed for the corresponding stilbene and tolane derivatives.[11-14] Similarly, the improved thermal stability realized by N-aryl substitution is not limited to nitro-substituted derivatives. In this regard, we have also demonstrated significant improvements in thermal stability for derivatives containing sulfonyl, di- and tricyanovinyl, barbiturate and thiobarbiturate and other strong electron acceptor substituents.[11] Although the magnitude of the improvement of thermal stability varies with the nature of the acceptor group and the electron transmitting functionality,[11-14] significant improvement is always observed for chromophores with arylamino donating substituents. Surprisingly, this also arises without significantly compromising the molecular hyperpolarizability of the chromophores as measured by EFISH techniques. This was rationalized both by finite field[18,19] and sum-over-states semiempirical calculations[20] and was verified by experimental measurements.[11] As a result of these investigations, we have prepared and characterized a number of NLO chromophores with both improved thermal stabilities and large nonlinearities. A representative list of these materials is shown in Table III together with their relevant thermal, spectroscopic properties and NLO properties. We have arbitrarily limited Table III to compounds with $T_d$ values (measured by DSC at a heating rate of 20°/minute) of greater than 320°C, and furthermore have included only examples where the calculated values of the reduced nonlinearity $(\mu \cdot \beta_{1300}(-\omega;\omega,0)/\mathrm{MW}$ are $\geqq 2.0 \times 10^{-30}$ $\mathrm{cm}^5$ ·D/esu. In this expression, MW is the molecular weight of the NLO chromophore. The calculated reduced nonlinearity is a particularly useful quantity for poled polymer applications at infrared frequencies. In this case, the molecular hyperpolarizability represents that for the electro-optic effect [i.e., $\beta(-\omega;\omega,0) \equiv \beta^{EO}$] extrapolated to 1300 nm. The quantity $\mu \cdot \beta_{1300}\ (-\omega;\omega 0)$ can be estimated from the zero frequency extrapolated hyperpolarizability $[\beta_0(-2\omega;\omega,\omega)]$ derived from EFISH measurements, assuming the validity of the two-state model.[21,22] The calculation of $u \cdot \beta_{130(}(-\omega;\omega,0)$ requires both a convention correction for the measured molecular hyperpolarizability determined by EFISH and an accurate value for the nonlinearity of the quartz standard.[8,23] We have recently proposed the reduced molecular nonlinearity (i.e., $u \cdot \beta_\lambda(-\omega;\omega,0)/\mathrm{MW}$) as an appropriate chromophore figure of merit for poled polymer applications.[14] Also included in Table III is a column for the calculated value of $r_{33}$ at 1300 nm. This value was based on a 50 wt.% loading level of the chromophore into Ultem polyetherimide and poling at 250°C with a poling field of 250 V/$\mu$m. In this case, the conversion of the chromophore nonlinearity measured by EFISH to an electro-optic coefficient at 1300 nm was calculated as described by Moylan et al.[8,14,23] The optical refractive index and the polymer dielectric constant were approximated as those for the polyether imide ULTEM.[9] By compromising slightly on the thermal stability requirement, many other diarylamino substituted materials with improved reduced nonlinearities are available.

Another useful feature of diarylamino substitution is the attending reduction in the volatility of the chromophores so that they may be studied conveniently by host-guest, variable temperature UV-visible spectroscopy. These data, for a number of the chromophores in Table III, are shown in Figure 5. Films containing 5 –7.5 wt.% of the respective chromophores in the host polyimide (ODPA-FDA) PI-1 (x = 0) were prepared by spinning the composites from 1,1,2,2-tetrachloroethane solution and baking to 250°C. The normalized absorbance at a particular processing temperature was determined by measuring the absorbance of the heated samples at the original $\lambda_{max}$ and dividing by the initial value measured for the sample cured at 250°C. All of the examples in Figure 5 were stable indefinitely at this lower temperature. The variable temperature studies were conducted at ~ 25°C heating intervals. The temperatures selected for the data presented in Figure 5 represent the lowest values where a significant change ($\geq 5\%$) in the absorbance was observed over the minimum measurement time interval (30 minutes). Although the problem of volatilization is reduced for these higher molecular weight samples, it cannot be eliminated entirely. At the lowest temperature for which detailed measurements were made (~ 275°C), all of the materials studied as guests in the polyimide host showed decreases in absorbance at the $\lambda_{max}$ of $\leq 15\%$ after 0.5h of heating. At 275°C, little change was observed in the spectra of **12**, **22**, **23** and **24**. At 300°C, only **22** and **24** showed $< 5\%$ absorbance loss after 0.5h of heating. At this higher temperature, volatility became an issue for the other samples as deduced from a careful analysis of the spectral data, which all showed a gradual decrease in absorption over the entire visible spectral region (390 –750 nm) without obvious changes in the peak shapes or the position of the peak maxima. Of the materials studied, only **19** showed spectral changes consistent with obvious decomposition, and these were apparent even at 277°C. The other chromophores appear to be lost at elevated temperatures primarily through volatilization. It is obvious that all of the chromophores studied show improved thermal stabilities in PI-1 relative to the materials in Table I, although **19** is clearly the least stable of the group, **12**, **19**, **22**, **23** and **24**.

### Thermal Stability Versus Chromophore Nonlinearity

Earlier we mentioned that a subsequent step in evaluating a promising NLO chromophore for high temperature applications is to determine the effect of heating the chromophore on the hyperpolarizability as subsequently determined by EFISH measurements in solution. For this procedure, neat samples were sealed in a glass tube and heated isothermally in a furnace to various temperatures for 30 minutes. The tube was then opened and diluted with chloroform to provide solutions which were studied both by EFISH and UV-visible spectroscopy. In the EFISH studies, the concentration dependence of the solution nonlinear susceptibility ($\Gamma$) of the chromophore was determined in chloroform solutions of samples which had been heated and compared with corresponding data for unheated samples (see Equation 1).[1] At the same time, the solution UV-visible spectra of the heated samples were recorded and the measured extinction coefficients at the original long wavelength $\lambda_{max}$ compared with those of the unheated controls. If a decrease in the extinction coefficient is also associated with a concurrent decrease in nonlinearity, both measurements should lead to similar conclusions. The results of these experiments for some representative NLO chromophores are shown in Table IV. Also included in the table for comparison are the corrected values of the quadratic molecular hyperpolarizabilities[8,23] measured prior to heating extrapolated to zero frequency ($\beta_0$) and the calculated reduced molecular nonlinearities[8,24,33] of the unheated samples. For most of the chromophores in Table IV, we have also included both the $T_d$ values (defined in the usual fashion and measured by DSC at a heating rate of 20°/minute) and $T_d^o$ values (obtained by extrapolation to zero heating rate). The latter are *always* substantially lower than the $T_d$ values measured at 20°/minute. The data reported in the last two columns refer to samples that had been heated to temperature for 30 minutes.

$$\Gamma = \gamma(2\omega;\omega,0) + \frac{\mu\cdot\beta}{15\mathrm{kT}} \qquad (1)$$

First, we see from Table IV that the results from the EFISH measurements and the UV-visible studies are usually comparable. Since the latter measurements are much easier to perform, we routinely use this technique for more extensive analysis of prescreened candidates. For our purposes, we have somewhat arbitrarily assumed that a viable use temperature in potential poled polymer applications is that temperature where 10% or less of the original chromophore nonlinearity (alternatively the decrease in the molar extinction coefficient at the original long wavelength $\lambda_{\max}$) is lost upon heating for 30 minutes. This time period is a reasonable interval based on current semiconductor processing. Although a 10% loss in the original NLO chromophore may seem minimal, we acknowledge that this change could significantly affect the linear optical losses and the waveguiding efficiency in a device. However, by this criterion, we can see from Table IV that only **9a**, **12** and **25** would be predicted to be useful for high temperature applications at 300°C. As mentioned earlier, the effective use temperatures for NLO chromophores are considerably lower than those predicted from simple onset decomposition values on model compounds measured at a heating rate of 20°/minute; often by 50–85°C. When the $T_d^o$ values are used instead, the predictions from DSC analysis correspond much more closely to the use temperatures suggested from the variable temperature EFISH and UV-visible studies. These results suggest that if DSC measurements are to be used as the sole criterion of thermal stability, the extrapolated values ($T_d^\circ$) should be employed. The data in Table IV indicate that **3**, **19** and **21** are the least thermally stable chromophores. They are also among the most nonlinear, on the basis of their reduced nonlinearities.

Table V contains collected thermal stability data for a number of chromophores studied by a variety of techniques. Also contained in the table are the temperatures for which heating for 30 minutes results in a 10% decrease in the magnitude of the decomposition endotherm as reported by Goldfarb et al.[7] The last column contains some data obtained for films where the related chromophore has been incorporated into a polyimide as a tethered substituent (vide infra). The temperature reported is that where a 10% decrease in the chromophore absorbance at $\lambda_{max}$ is observed after 30 minutes of heating. In a number of cases, the chromophore appears to be stabilized somewhat relative to the model chromophore by incorporation into the polymer.

## TETHERED NLO POLYIMIDES

Given the improved thermal stability of diarylamine substituted chromophores, we have developed a number of routes to materials of this type. For tethered substituents, the chromophores may be attached to the oxygen of 3,5-diaminophenol by either SN-2 displacement from N-tosyloxyalkyl substituted chromophores[24] or by Mitsunobu coupling[24,25] of the N-hydroxyalkyl substituted derivative (M2-M5). In the latter case, the amino groups of the phenol were first protected as the bis-trifluoroacetamide, and the amino substituents liberated after coupling by treatment with $K_2CO_3$-methanol-water. The monomer M2 is included as an example containing an alkyl amino donor substituent, while the others contain triarylamino substituted donors. M5 contains two NLO groups/diamine in an effort to increase the chromophore density in the polymer. Alkyl tethers seem not to effect the stability of the chromophore as long as they are not directly attached to the donor nitrogen.

The desired polyimide derivatives were prepared by condensation polymerization as shown in Scheme 1. The initial polyamic acids PAA 2-4 could be spun onto a substrate and cured by ramping the temperature to 260°C. For those examples where $X=(CF_3)_2C$, the polyimide derivatives were soluble in organic solvents. These materials were usually spun in the preimidized form. The improved thermal stability of the arylamino substituted chromophores tethered to the polyimide backbone is shown in Figure 6. The onset decomposition temperature measured by DSC of the aryl substituted polymer **PI-3b** is almost 40°C higher than that of **PI-2b**. Likewise, this stabilizing effect is apparent by variable temperature UV-visible spectroscopy studies of the polymer films. In this case, the absorbance at the $\lambda_{max}$ of the chromophore was monitored versus time at a variety of temperatures and the results shown in Figure 7. In each case, the heating was conducted under an inert atmosphere. Plots such as these are the origin of the data shown in the last column of Table V.

### Nonlinearity Measurements

The electro-optic coefficients ($r_{33}$) for the polymers **PI-2** through **PI-5** were measured by one of three procedures depending on the poling technique, and the results are shown in Table VI. For samples that were poled by corona discharge, an attenuated total reflection (ATR) technique was employed.[26] When single films were electrode poled, an ellipsometry technique was utilized.[27,28] A heterodyne technique[29,30] was used to determine $r_{33}$ of polymers poled in modulator geometries. With the second method, rather thin films (NLO polymer layer only) were utilized (1.5 –2.5 $\mu$m) and the poling field was maintained at a relatively low and constant value (~ 75 V/$\mu$m) to avoid any possibility of shorting and damage to the film. The values of the electro-optic coefficient ($r_{33}$) obtained in these electrode poling experiments would be expected to increase linearly with field.[1] In the case of **PI-3b**, a triple-stack phase modulator composed of two crosslinked acrylate buffer layers sandwiching the NLO polymer layer was constructed and larger poling fields were applied (~ 250 V/$\mu$m). The $r_{33}$ value measured in this modulator was similar to those obtained both by corona poling and by single polymer layer ellipsometry after extrapolating the latter to the modulator poling voltage. In the case of two related NLO polyimides, the $r_{33}$ values measured either at 250 V/$\mu$m and/or extrapolated to this poling field compared quite favorably with those predicted by calculation[31] (i.e., 8.8 pm/V for **PI-3a** and 8.3 pm/V for **PI-3b**, respectively). However, the measured value for the 6-nitrobenzothiazole polymer **PI-4b** seems anomalously low based on the substantially larger hyperpolarizability of the chromophore.[11] Rough calculations of the $r_{33}$ value predicted for this polymer indicated an expected value of around 20 pm/V at 250 V/$\mu$m considerably larger than the initial experimental value. It is possible that the poling is less efficient for this more extended chromophore.

Greatly improved thermal orientational stability for the polyimides **PI-2–PI-4** would be anticipated by virtue of their relatively high glass transition temperatures (see Table VI). Relaxation data obtained by monitoring the intensity of the second harmonic signal of films of **PI-3a** and **PI-3b** poled in a corona field (~ 250 V/$\mu$m, poling temperatures 210–220°C) are shown in Figure 8.[24] After a small decay in the signal of ~ 5%, each sample was stable for over 1000h at 100°C. In addition, preliminary results suggest that annealing the sample of **PI-2b** at 175°C for ~ 3 hrs in the poling field increases the characteristic relaxation time $\tau$ (derived from a stretched exponential fit[1] of the decay data) by ~ 50%.

## EMBEDDED DONOR POLYIMIDES

Thus far we have been discussing only NLO polyimide derivatives which contained the active functionality tethered to the main chain as a pendant substituent. Although the thermal and oxidative stability of these materials are relatively good and the orientational stability is adequate at 100°C , the Tg's of these materials are below 230°C. Since the processing temperatures for complete on chip integration will often exceed 250°C, NLO polymers with Tg values in excess of this temperature will be required. It seems unlikely that this goal will be achieved with any processable NLO polyimides containing the NLO chromophore attached via a flexible tether. To date, no polyimide derivatives of this type with a Tg value exceeding 250°C has been reported and most NLO polyimide derivatives cluster in the 200–230°C range.[32] In an effort to raise the glass transition temperature of NLO polyimides, we considered derivatives where the chromophore was incorporated into the main chain via either the donor or acceptor functionality. This type of bonding should increase the polymer rigidity but still maintain adequate polymer flexibility to allow poling. It was anticipated that polyimides containing the chromophore incorporated into the main chain through both donor *and* acceptor bonding would result in main chain polymers which would be difficult to pole.

Initially, it was decided that the donor substituent should contain the aromatic diamine functionality necessary for polymerization. However, the target monomer M-6 proved impossible to prepare by classical electrophilic substitution reactions. All attempts to couple triarylamines substituted with peripheral electron donor groups with diazonium salts failed and resulted instead in dearylation.[24] The desired monomer M-6 was finally prepared by the Mills reaction of tris-p-aminophenylamine with substituted nitrosobenzene derivatives as shown in Scheme 2.. This is an exceptionally versatile synthetic procedure limited only by the ability to prepare the substituted nitrosobenzene partner.

The embedded donor polyimides were prepared by the classical condensation route shown in Scheme 3.[33] The flexibility of the polymer could be tuned somewhat by the selection of the dianhydride. Although a wide variety of soluble polyamic acids could be prepared by this method, in practice most of the polyimide derivatives were insoluble in common organic solvents. The two derivatives (**PI-6** and **PI-7**) were both processable in the imidized form. The increased flexibility provided by the use of the anhydride **26b** was evidenced by the lower Tg of **PI-7** (255°C) compared with the more rigid derivative **PI-6** (350°C).

The NLO chromophore in **PI-6** was exceptionally thermally stable as shown by the DSC data presented in Figure 9. For comparison, related data for two tethered examples (**PI-2b** and **PI-3b**) are included in the figure. The films of **PI-6** were also exceptionally stable and no change in the absorbance at the $\lambda_{max}$ (374 nm) of the chromophore was evident even after several hours at 350°C. Figure 10 shows the stability of **PI-6** monitored by UV-visible spectroscopy in comparison with other tethered NLO polyimides. The more flexible derivative **PI-7** was also very stable, albeit somewhat less so than **PI-6**. Variable temperature UV-visible spectroscopy of **PI-7** showed less than 10% decrease at the $\lambda_{max}$ after 1h at 300°C. Significant loss in absorbance (22%) was observed after 0.5h at 330°C. The results from DSC studies corroborated the UV-visible findings. It is believed that the alkyl spacer groups and the ester functionality in **PI-7** are the ultimate source of the instability.

Both the **PAA-6** and the imidized form could be oriented by electrode poling. The former was poled by ramping the temperature slowly from 150–250 or 280°C.[33b] The decay of the orientated samples while heating at 3°/minute is shown in Figure 11. The lower orientational stability of the samples derived from the polyamic acid relative to the polyimide itself is believed to result from the lower cure temperature used for the PAA derivatives. Extrapolation of the decay curve from **PI-6** poled at 300°C intersects the temperature axis around 360°C which is close to the measured polymer Tg (i.e., 350°C).

The thermal stability of the polar order of **PI-6** is unprecedented for a thermoplastic material. The decay at a variety of temperatures is shown in Figure 12. The material is stable indefinitely at 250°C and shows only about 12% loss after 0.5h at 300°C. Above 300°C the loss of polar order occurs rapidly as the Tg of the polymer is approached. **PI-7** is less orientationally stable, as expected from its lower Tg value (255°C). This material is stable indefinitely at 200°C and shows only 12% loss after 0.5h at 220°C. Approximately 50% of the original nonlinearity remains after 0.5h at 240°, a temperature only 15°C below the Tg. The measured $r_{33}$ values for **PI-6** (poled 300°C) and **PI-7** (poled 255°C) were 5 and 6 pm/V respectively (1.3 $\mu$m). The poling electric field strength varied from 160–180 V/$\mu$m. Relaxation of the poled NLO chromophores was followed by monitoring the decrease in the SHG signal emanating from the samples as a result of the decay in the poled order. The observed decay can be fit quite well by a stretched exponential function.[1] Figure 13 shows the variation of the characteristic decay time $\tau$ (point at which the second harmonic coefficient (d) has decayed to 1/e of its initial value) with temperature for **PI-6, PI-7** and the tethered derivative **PI-3b**. The stability of the embedded derivatives are evident from the much larger values of $\tau$ relative to **PI-3b** at elevated temperatures.

Electric field poling at very high temperatures is exceedingly demanding and requires highly purified polymer samples. In the case of **PI-6**, this required multiple reprecipitations, isolation and drying. The samples, after spinning from cyclopentanone, were dried in a vacuum oven at 200°C for several hours. Even after rigorous purification, the conductivity of the samples increased rapidly as the poling temperature exceeded 300°C. These data are shown in Figure 14. Prolonged heating above 300°C led to substantial resistive heating leading ultimately to a thermal run away and sample breakdown. The intensity of the second harmonic signal for a sample of **PI-6** heated to the glass transition temperature increased with the applied field. The square root of the second harmonic signal was, as expected, linear with the applied field. These data are shown in Figure 15. Also shown in the same figure is the power dissipated (mW) with increasing electric field. At a field of 220 V/$\mu$m, breakdown and shorting occurs resulting in a catastrophic drop in the second harmonic signal due to rapid orientational relaxation, since the polymer is held near the Tg in the absence of a significant poling field.

We have studied the high temperature poling behavior of **PI-6** in some detail. Figure 16 shows the generated second harmonic signal as a function of temperature (heating rate ~ 8°/min.). At the onset of the experiment, the sample temperature was 250°C and the second harmonic signal increases with temperature until the sample reached 350°C. At this point, where the current increases significantly, the heater was turned off. Over a space of 2–3 minutes, the second harmonic signal increases by a factor of two and the sample shorts. This increase in signal is apparently due to the increased applied electric field when the sample conductivity decreases as the sample begins to cool. Some of the increased signal upon cooling is undoubtedly due to the increased contribution from third-order processes as the field increases. After the sample is shorted, it is not possible to measure the electro-optic coefficient, but the second harmonic coefficient can still be estimated since it doesn't require a field across the sample. The $r_{33}$ value just prior to shorting was ~ 4 pm/V (1.3 $\mu$m). If we assume a normalized second harmonic coefficient of 1.0 at this point, we estimate that this value increases by a factor of 3–4 immediately after shorting. This would suggest that the $r_{33}$ value at this point, if it could be measured, could be as high as 12 pm/V (1.3 $\mu$m ) This is not an unreasonable value since, based on the measured nonlinearity of the chromophore, a weight % of 47% for the NLO chromophore in the polymer, and using standard values for the refractive index and the dielectric constant based on those of an isotropic model polyimide such as ULTEM, a calculated $r_{33}$ value at 250°C (250 V/$\mu$m) was estimated to be around 11 pm/V.

We have demonstrated that poling nonlinear polymers at very high temperatures near the glass transition temperature of the polymer can be very difficult due to conductivity effects which result in a decreased field across the NLO layer and cause significant resistive heating. For the construction of waveguide devices from high Tg polymers, the situation is also exacerbated by the need to find buffer layers with thermal and mechanical stability at the poling temperature which also have the proper electrical characteristics. In this regard, the buffer layers must be somewhat conducting, but the resistance must be such at the polymer poling temperature that most of the applied voltage is dropped across the NLO layer. This is a serious materials challenge for the construction of operating devices from high Tg thermoplastic NLO polymers.

Another difficulty which will be encountered in trying to make waveguiding modulators and switches from high Tg NLO polymers is that the optical losses (scattering and absorption) must remain low after poling. This is certainly a nontrival problem, and we find that the losses always increase, sometimes significantly so, upon heating to high temperatures even without poling. These effects are not always detectable by monitoring the polymer UV-visible absorption spectrum before and after heating. This effect is shown in Figure 17 for **PI-4**. The top shows the UV-visible spectra of the polymer before and after heating to 250°C. This is consistent with the earlier observation that the polymer film shows only a 10% decrease in the absorbance at the $\lambda_{max}$

even after 0.5h at 282°C. On the other hand, part B of Figure 15 shows the photothermal deflection spectra (PDS)of the same polymer after heating at various temperatures for 0.5h. At 1300 nm (see vertical line), the absorbance has already changed by almost two orders of magnitude after heating to 250°C and significant changes are observed even at lower temperatures. Although **PI-4** may be somewhat more sensitive than many high temperature NLO polymers, we believe that the results presented are not atypical and one can expect increased losses upon heating to the elevated temperatures necessary for electric field poling in high Tg NLO polymers.

## PHOTOASSISTED ELECTRIC FIELD POLING

The difficulties associated with polymer poling at high temperatures (i.e., increasing conductivities, lack of suitable buffer layers and increased optical losses) has led us to explore other techniques that might be useful for poling high temperature polymers. We now report[34] very preliminary results on the photoassisted electropoling (PEP) of a high Tg NLO polyimide which suggest that the technique might have some utility.

The photoisomerization of trans azo derivatives to the cis isomer is facile and is both photochemically and thermal reversible. The latter is particularly fast for donor-acceptor substituted derivatives. The rapid, reversible isomerization leads to substantial movement of the chromophore from its initial position in the film prior to irradiation. Irradiation of a film with polarized light (linear or circularly) leads to the rapid development of considerable birefringence. When an electric field is simultaneously applied, polar order is induced parallel to the propagating direction of the irradiating light. We have performed one study with a high Tg NLO polymer to look for photo-orientation far below the polymer Tg.[34] For this we have chosen **PI-2b** which has a glass temperature of 210°C. Irradiation perpendicular to the film surface with circularly polarized light at room temperature results in the development of polar order normal to the film surface. The results of this very preliminary experiment are shown in Figure 18. After irradiation at room temperature at applied field of 135 V/$\mu$m, an $r_{33}$ value of 31.5 pm/V was measured (633 nm). Extrapolation of this electro-optic coefficient to 1.3 $\mu$m would predict a value of ~9 pm/V. This value is actually slightly larger than that obtained by electrode poling when the actual measured value (75 V/$\mu$m, 1.3 nm) is linearly extrapolated to a poling field of 135 V/$\mu$m. In the case of **PI-2b**, efficient photoassisted poling was observed at a temperature almost 190°C below the polymer Tg! This exciting, albeit very preliminary, result suggests that PEP techniques might be useful for poling very high Tg azo containing NLO polymers at modest temperatures, far below the polymer glass temperature, thereby avoiding some of the significant drawbacks of thermal electric field poling. More work is definitely needed in this area.

## SUMMARY

In summary, we have developed a useful thermal protocol for testing the viability of NLO chromophores for high temperature polymer applications. In our chromophore studies, we have found that the nature of the donor substituent is more important for determining thermal stability than the acceptor group, at least for standard electron transmitting connecting bridges. In this regard, for amino donors, aryl substitution *always* leads to significant improvements in thermal stability relative to alkyl substituted derivatives. Using this screening protocol, we have identified a number of highly nonlinear chromophores with acceptable thermal stabilities. A number of these were incorporated into polyimide derivatives as tethered substituents to yield high Tg NLO polymers. The orientational stabilities of these tethered materials at 100°C were adequate for device applications. NLO polyimides with much higher Tg's ranging from 250—350°C were prepared by embedding the donor substituent into the polymer main chain. The thermal and oxidative stability of these materials were extraordinary (300—350°C) and orientational stability up to 300°C was observed for one of these materials. This greatly exceeds that of any NLO poled polymer reported, including examples which have been heavily crosslinked. Finally, preliminary results suggest that photoassisted electric field poling (PEP) of polymers containing azo chromophores at temperatures far below the polymer glass temperature may provide a solution to the difficulties inherent to thermal poling at very high temperatures.

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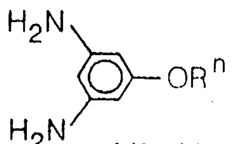
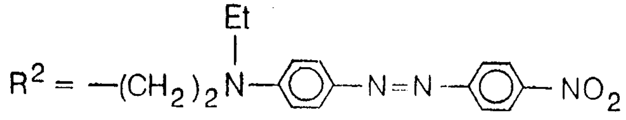
## Structures



M2 - M4

M2



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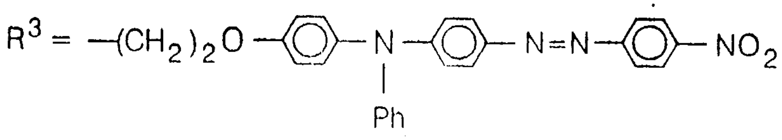

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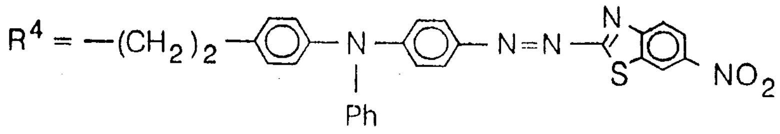

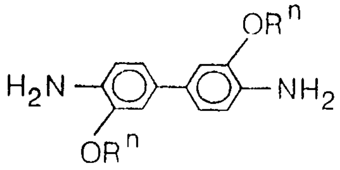

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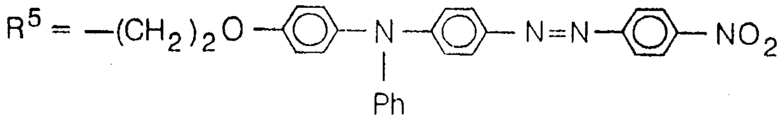


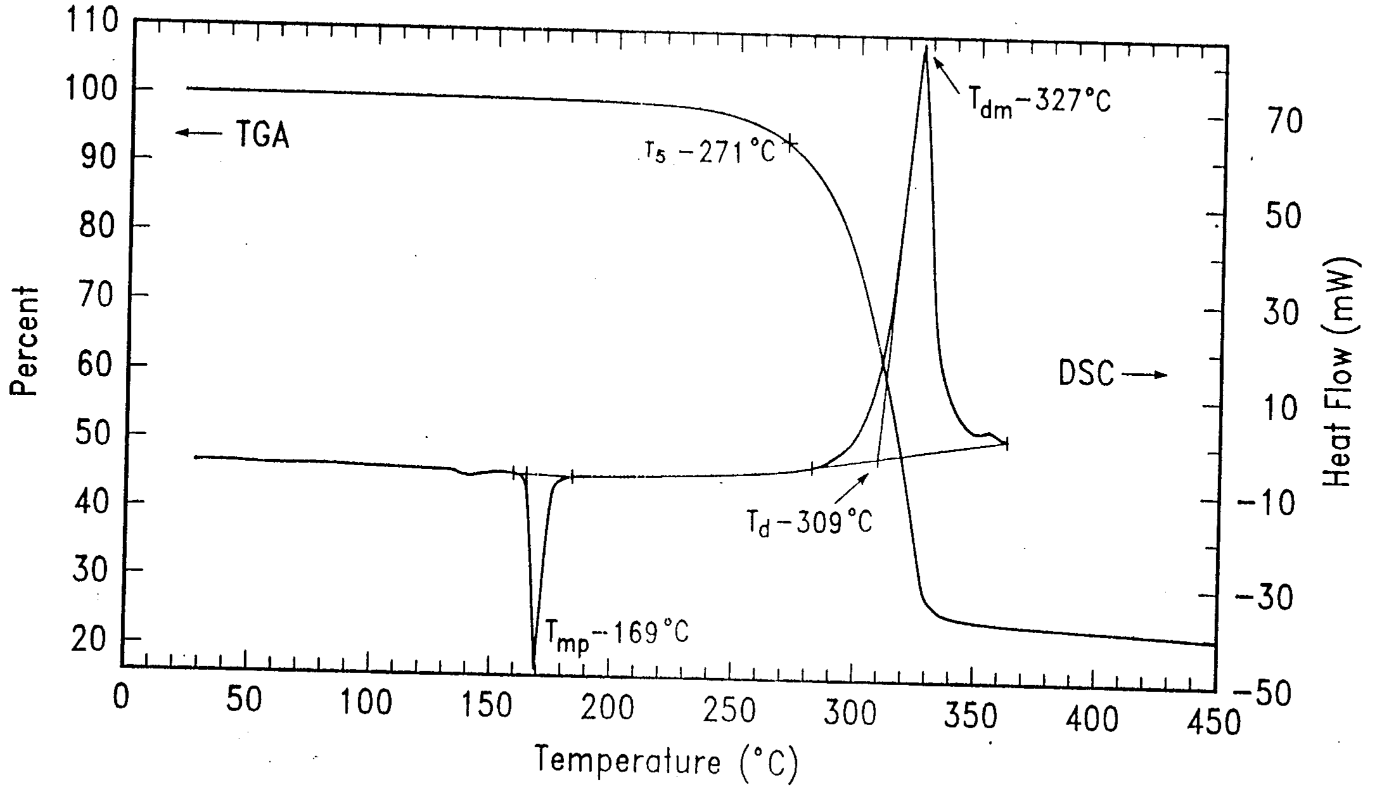


Figure 1. TGA and DSC traces of DR1 (1) recorded at a scanning rate of 20°/minute.

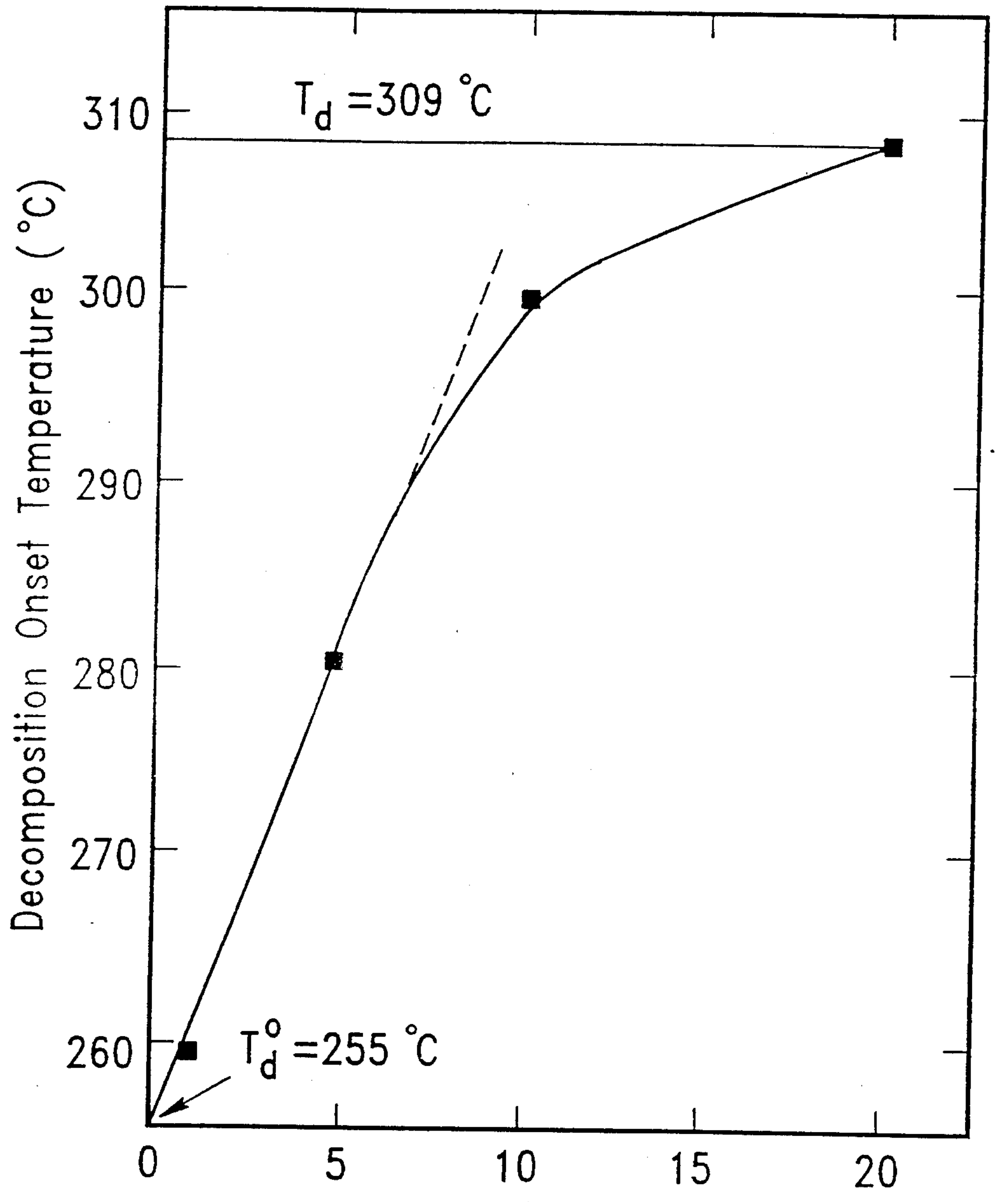


**Figure 2.** Variation of the onset decomposition temperature of DR1(**1**) with heating rate.

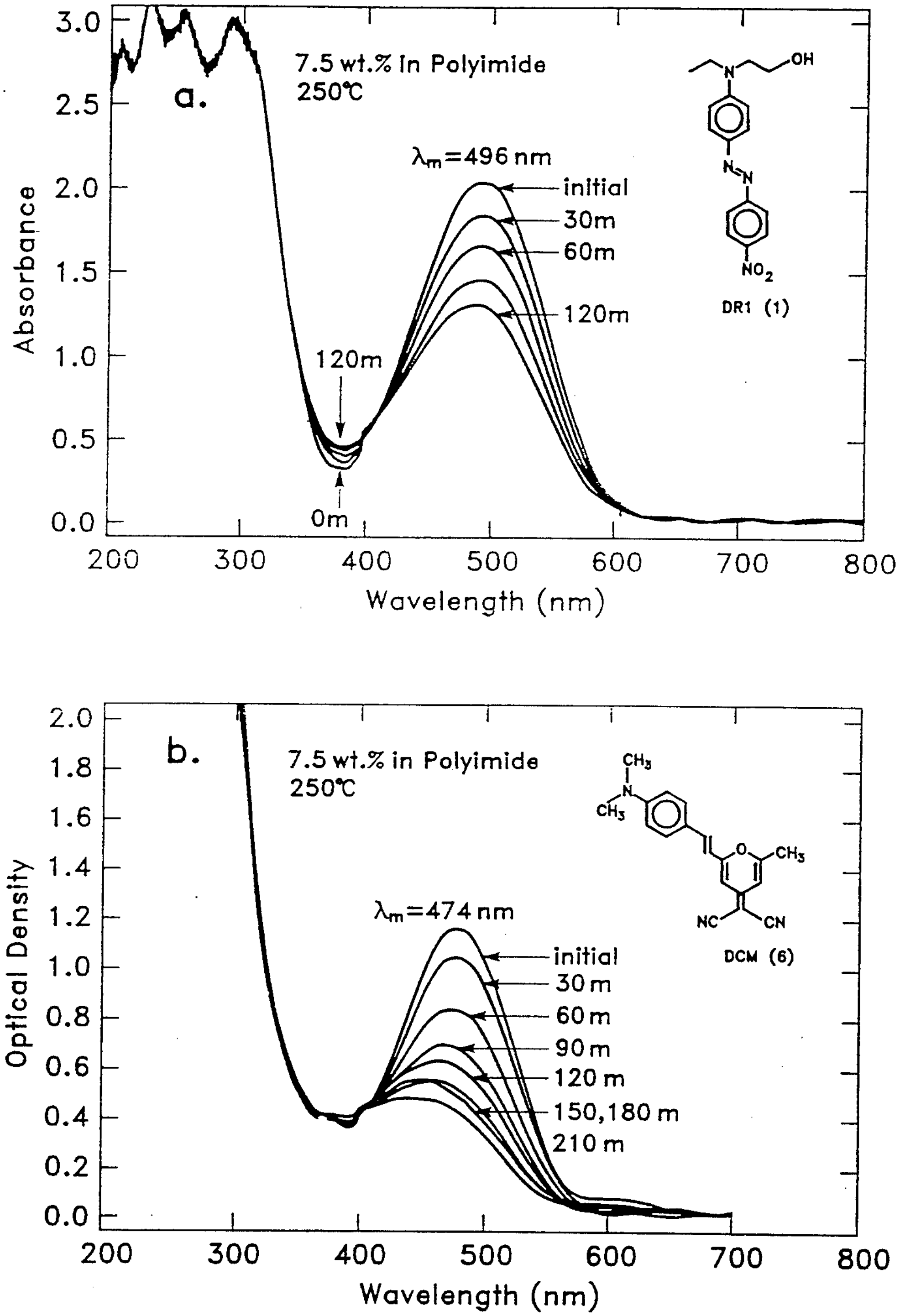


**Figure 3**. High temperature (250°C) UV-visible studies of host-guest composites. (a) DR1 (**1**) in PI-1 (x = 0). (b) DCM (**6**) in PI-1 (x = 0).

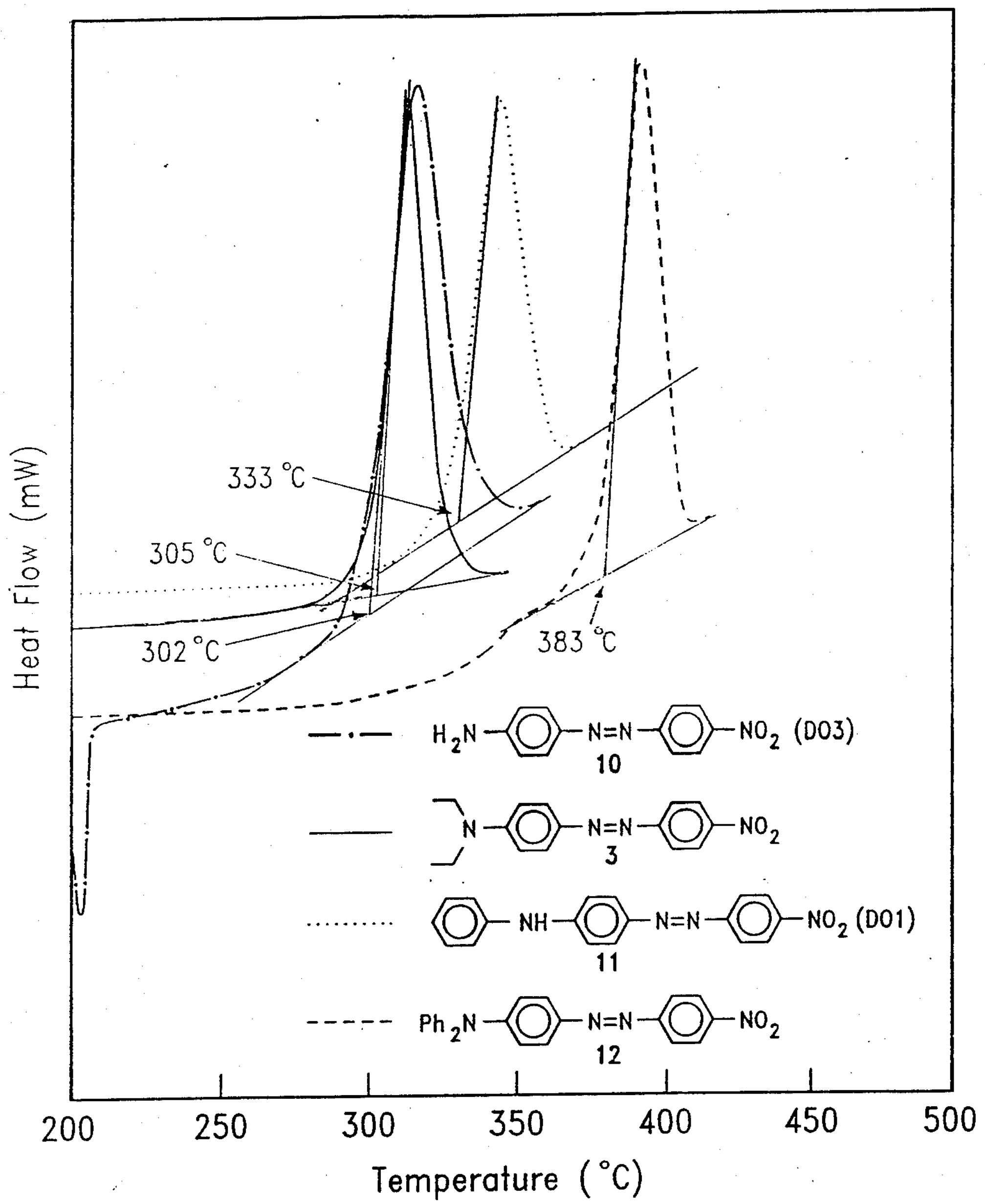


**Figure 4.** DSC analyses of a number of N-substituted-4-amino-4′-nitroazobenzene chromophores, scan rate 10°/minute.

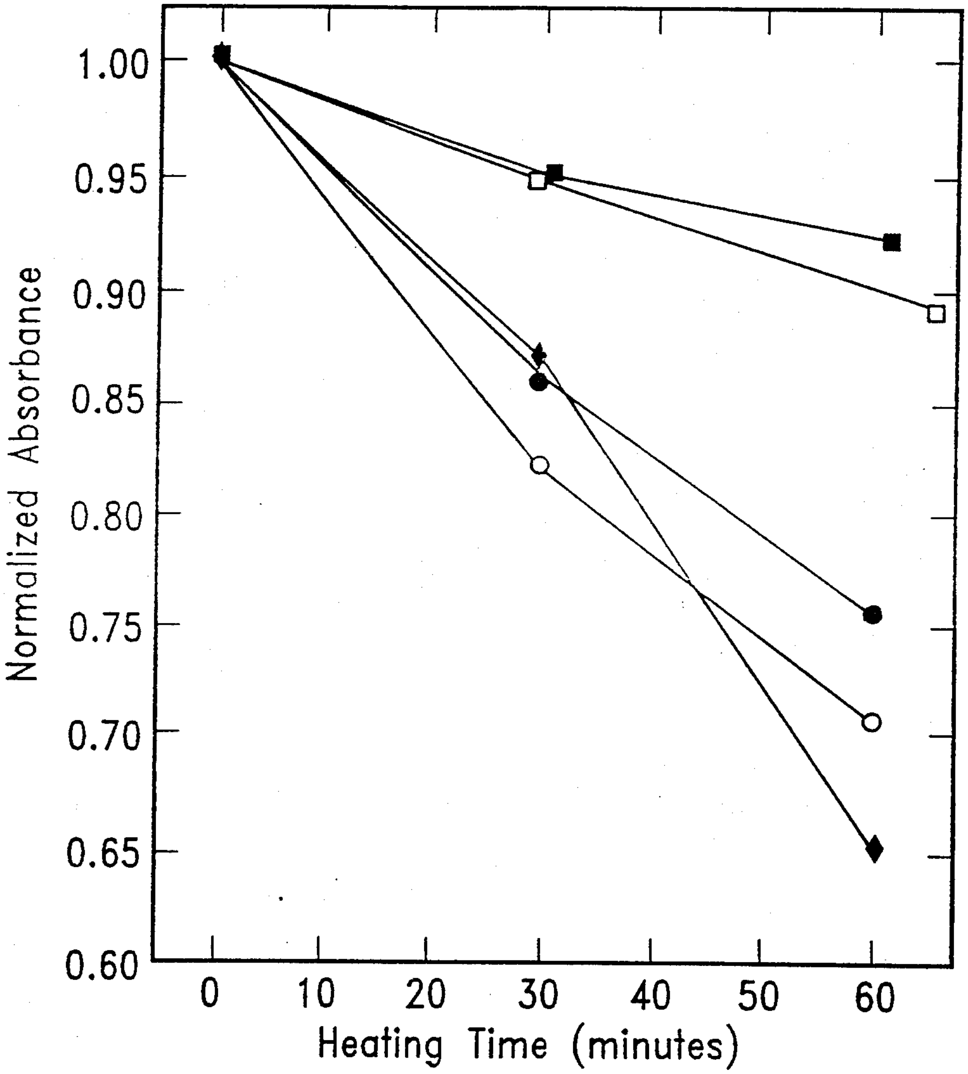


**Figure 5.** Variable temperature UV-visible studies of host-guest composites containing an NLO guest dissolved in PI-1 (x = 0). (a) -■-, **24**, 299°C, (b) -□-, **23**, 277 C, (c) -●-, **19**, 277°C, (d) -○-, **12**, 299°C, (e) -♦-, **25**, 328°C; temperatures measured directly on the quartz wafer with an attached thermocouple.

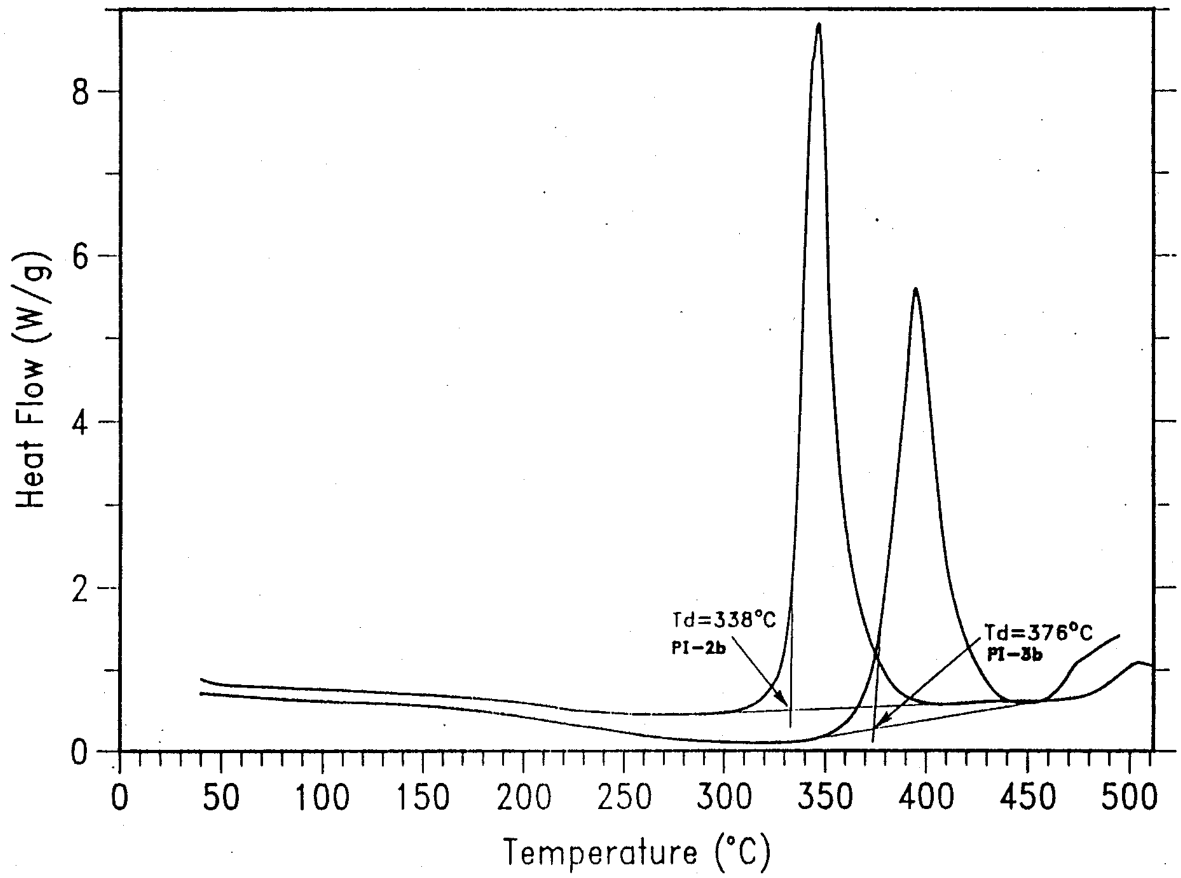


**Figure 6**. DSC analysis of the polyimides **PI-2b** and **PI-3b** measured at a heating rate of 20°C/minute.

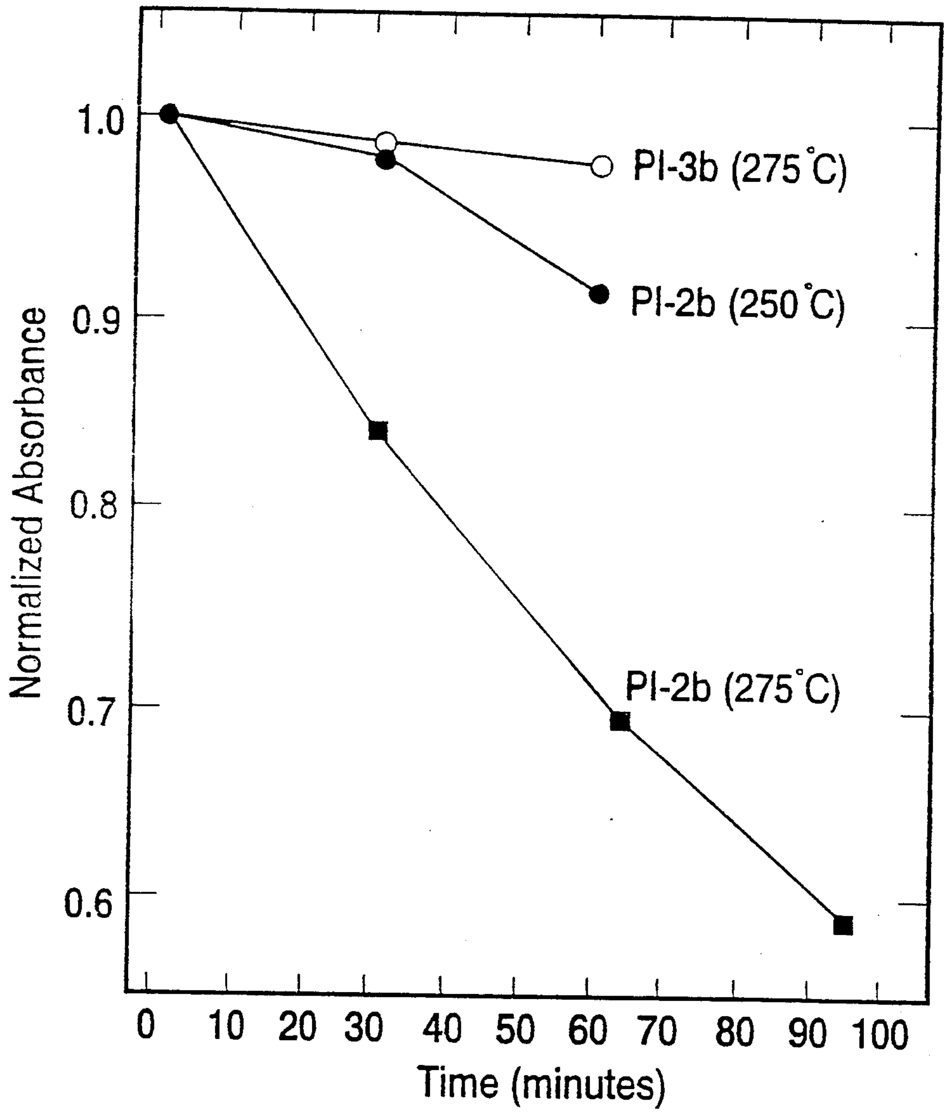


**Figure** 7. Variable temperature UV-visible studies of films of **PI-2b** and **PI-3b**. Absorbance measurements were made at the $\lambda_{max}$ of the long wavelength transition (474 nm for **PI-2b** and 498 nm for **PI-3b**).

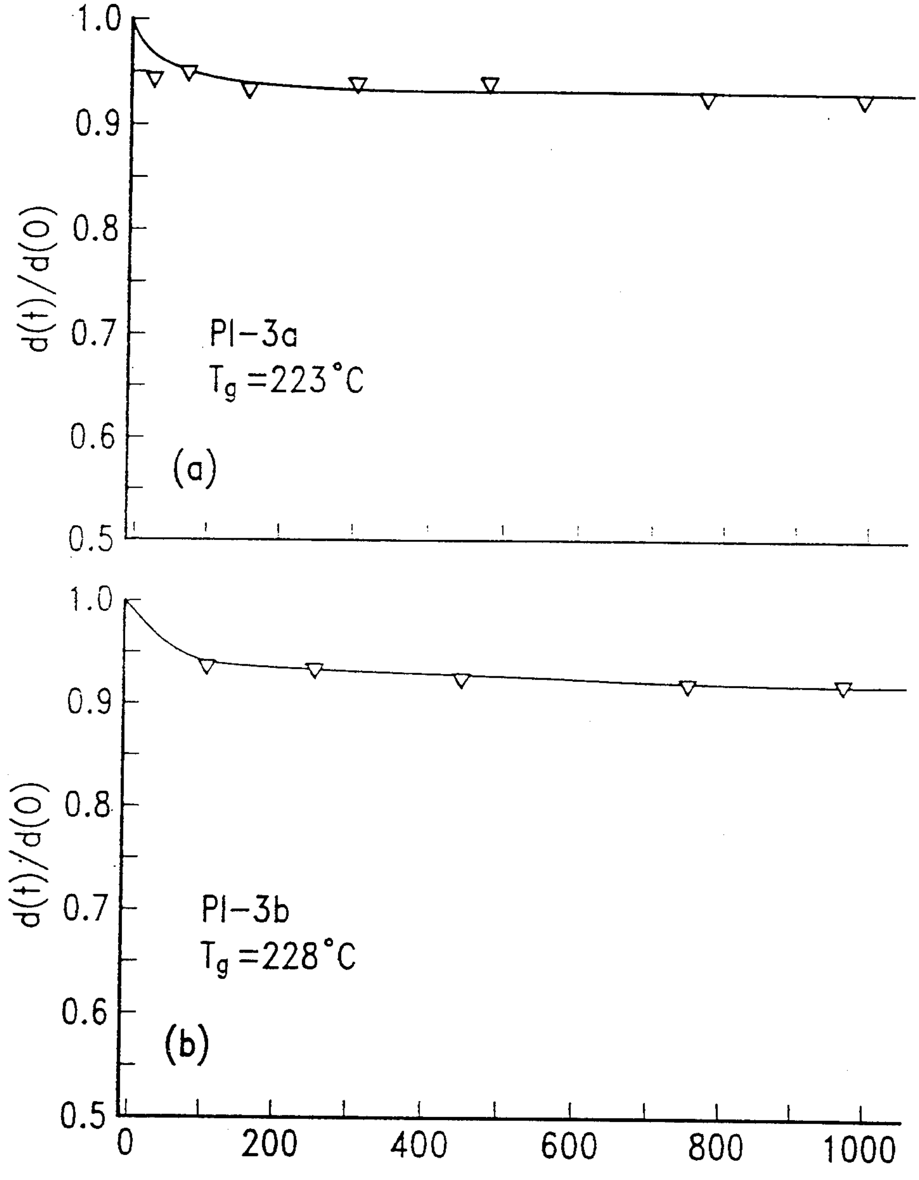


**Figure 8**. Decay in the second harmonic coefficient at 100°C, laser fundamental 1.047 $\mu$m: a. **PI-3a**, Tg = 223°C; b. **PI-3b**, Tg = 228.

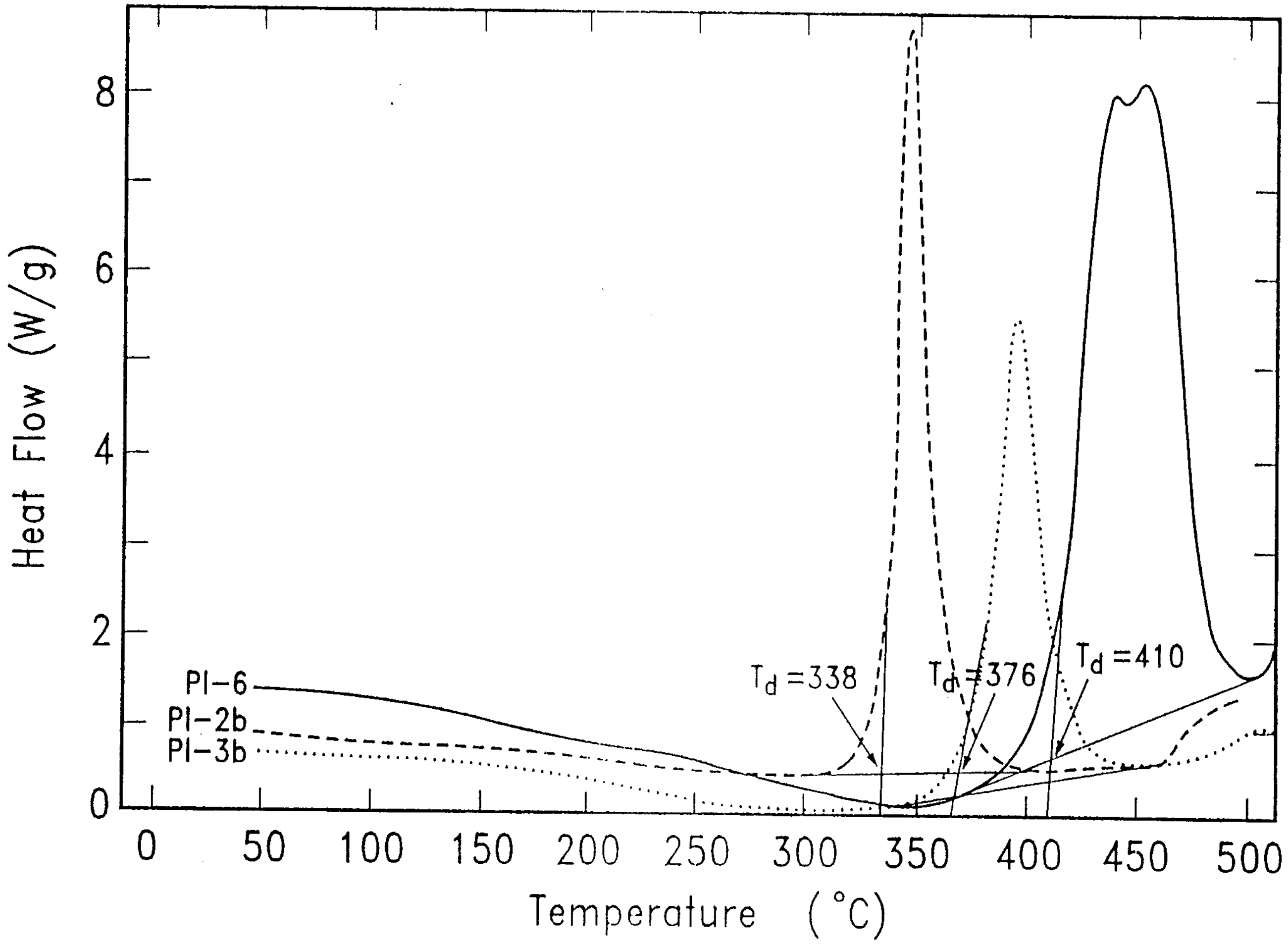


**Figure 9**. Thermal stability of NLO polyimides by DSC analysis (scanning rate 20 /minute):

(—) **PI-6**, (---) **PI-2b**, (···) **PI-3b**.

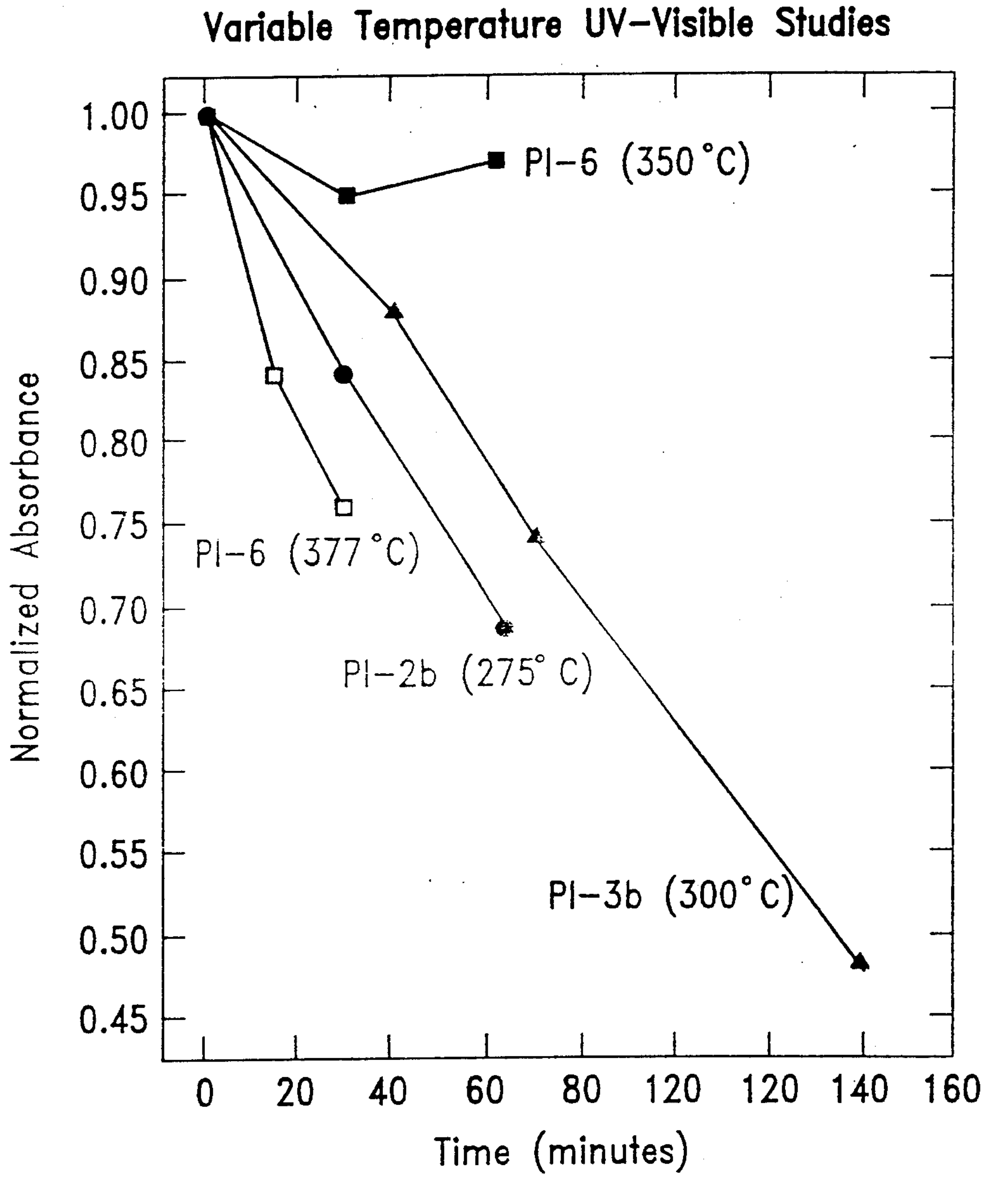
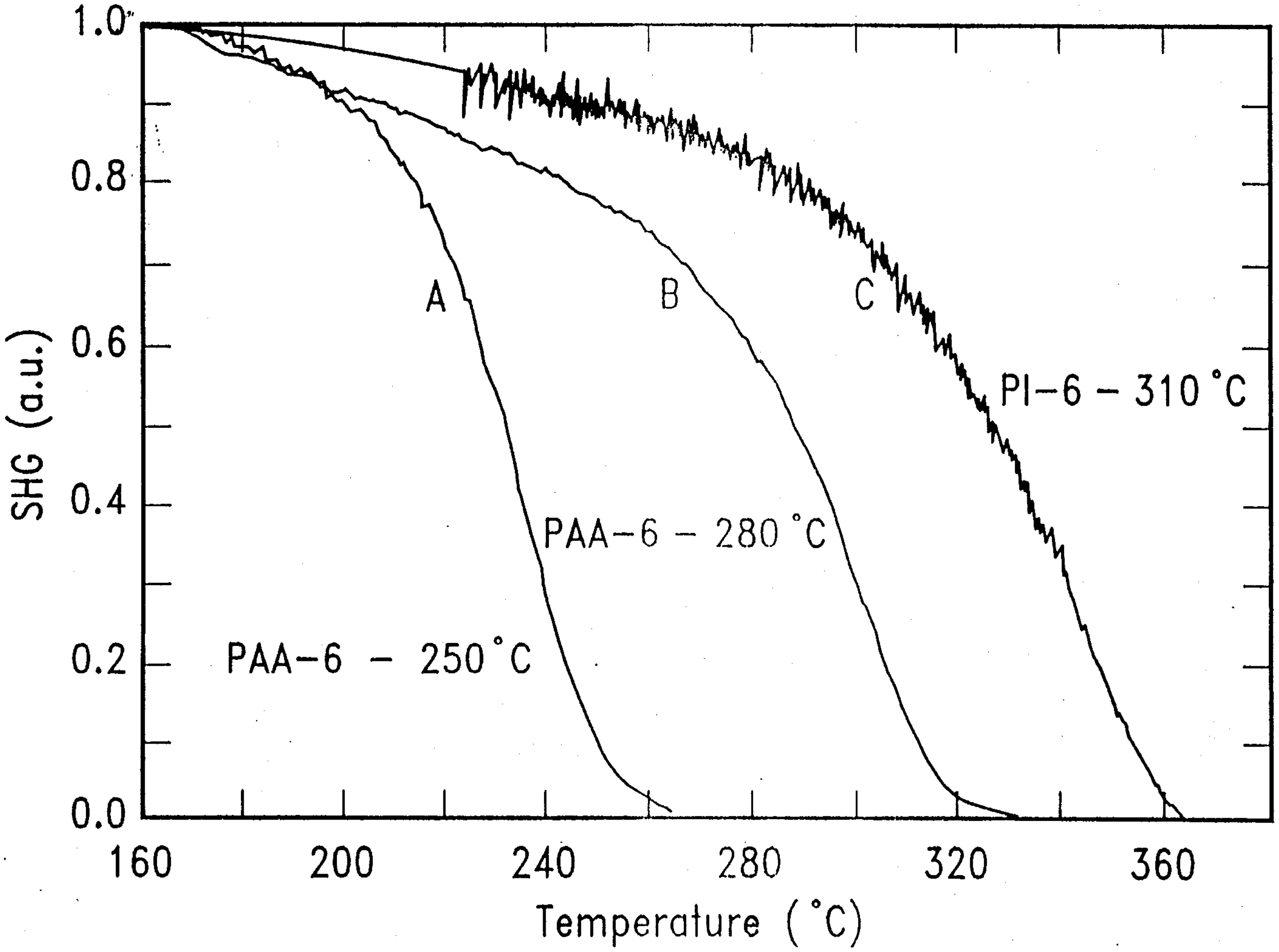


**Figure 10**. Variable temperature UV-visible studies of a variety of NLO polyimides: (-■-) **PI-6** (350°C), (-▲-) **PI-3b** (300°C), (-●-) **PI-2b** (275°C), (-□-) **PI-6** (377°C). Temperatures were measured on the wafer and the absorbance was recorded at the $\lambda_{max}$.

**Figure 11**. Polar order stability as determined by thermal ramping (rate 3°/minute); laser frequency fundamental 1.047 $\mu$m. (a) Film prepared from the poly(amic acid) **PAA-6** heated to a maximum temperature of 250°C in a corona field; (b) film prepared from the poly(amic acid) **PAA-6** heated to a maximum temperature of 280°C in the corona field; (c) chemically imidized film of **PI-6** poled at 310°C (corona field).



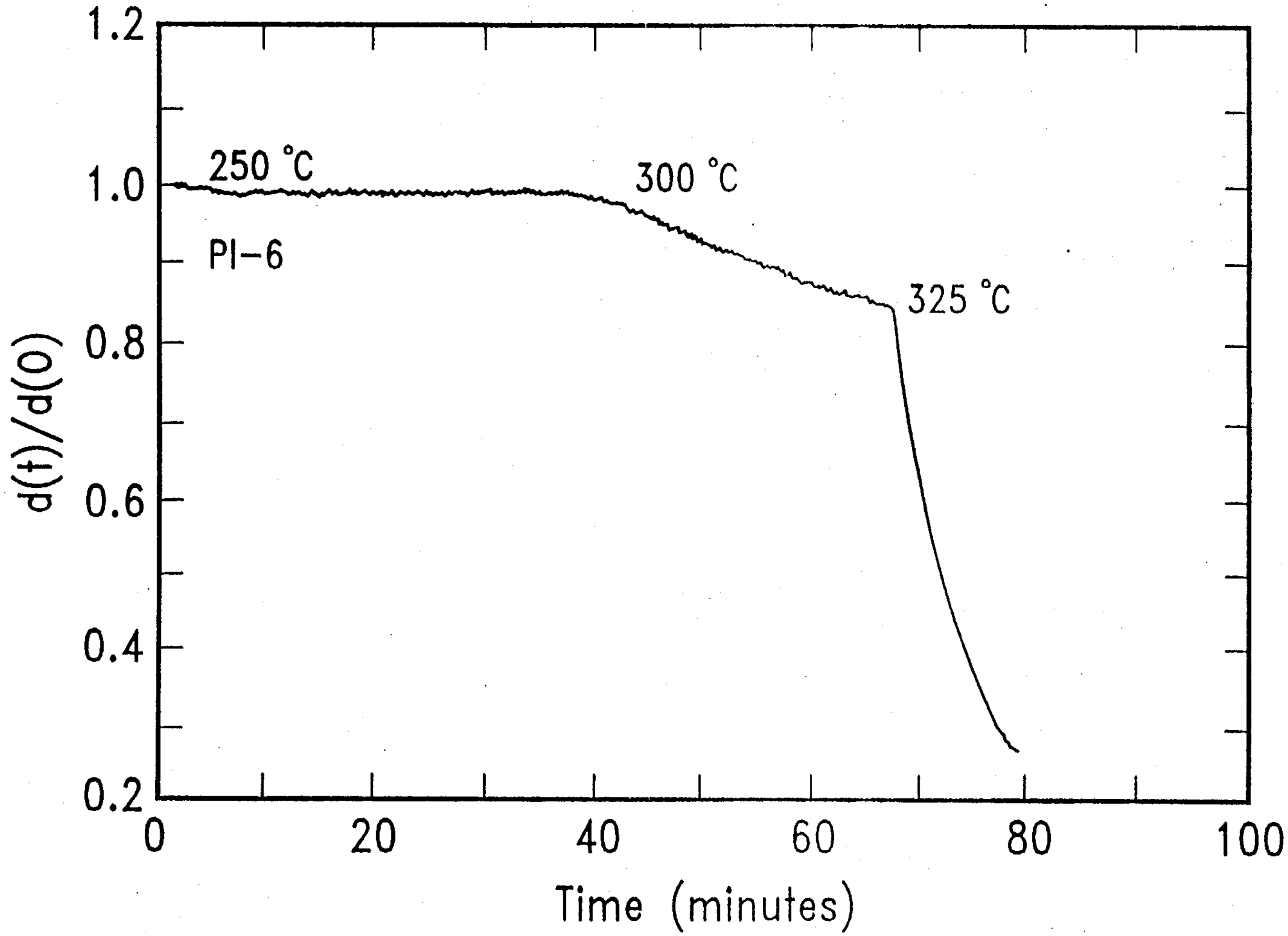


**Figure 12.** Polar order stability of **PI-6** at various operating temperatures. The interval at each temperature was 30 minutes.

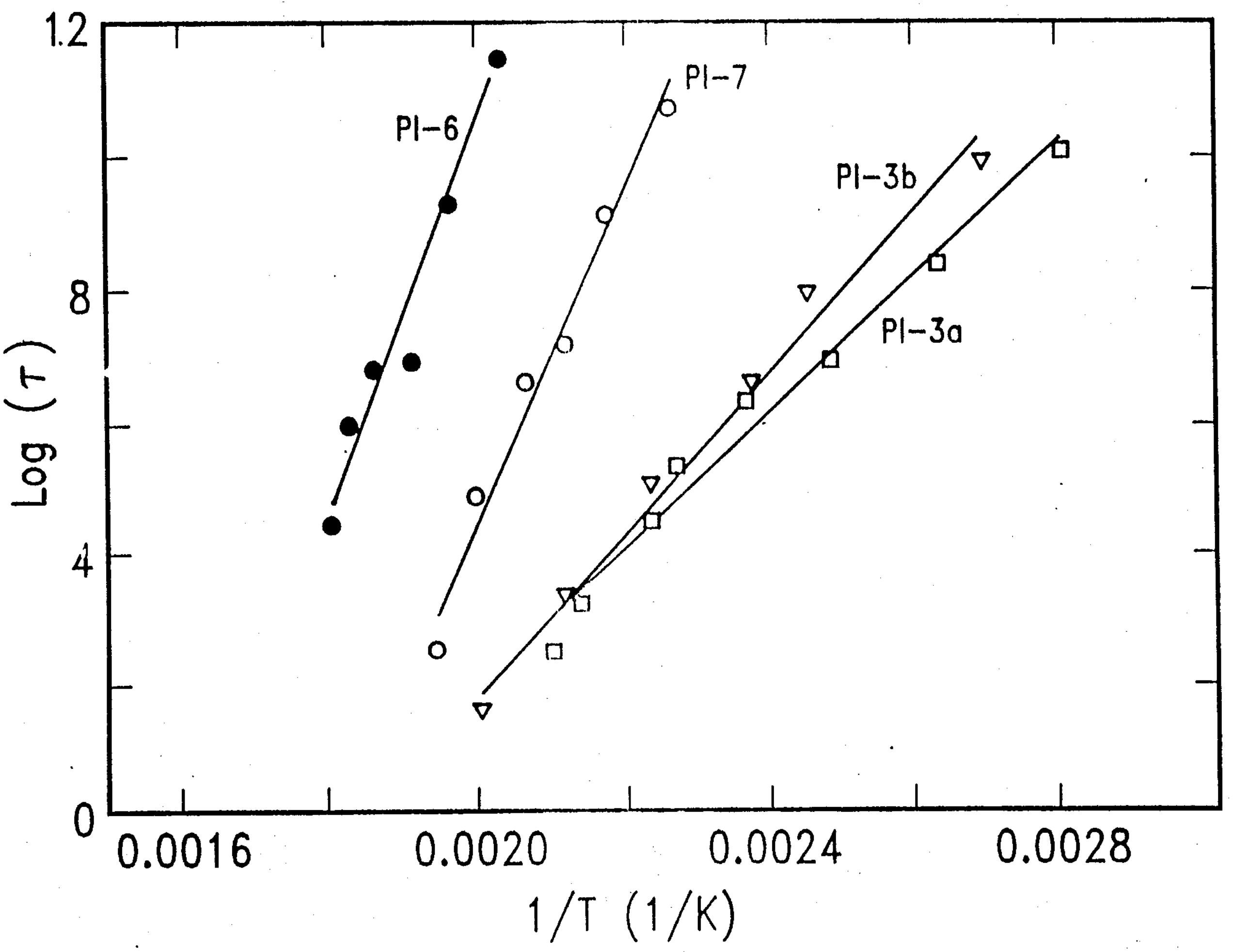


**Figure 13**. Arrhenius plots for some tethered and embedded donor NLO polyimides: (-●-) **PI-6**, (-○-) **PI-7**, (-▽-) **PI-3b**, (-□-) **PI-3a**.

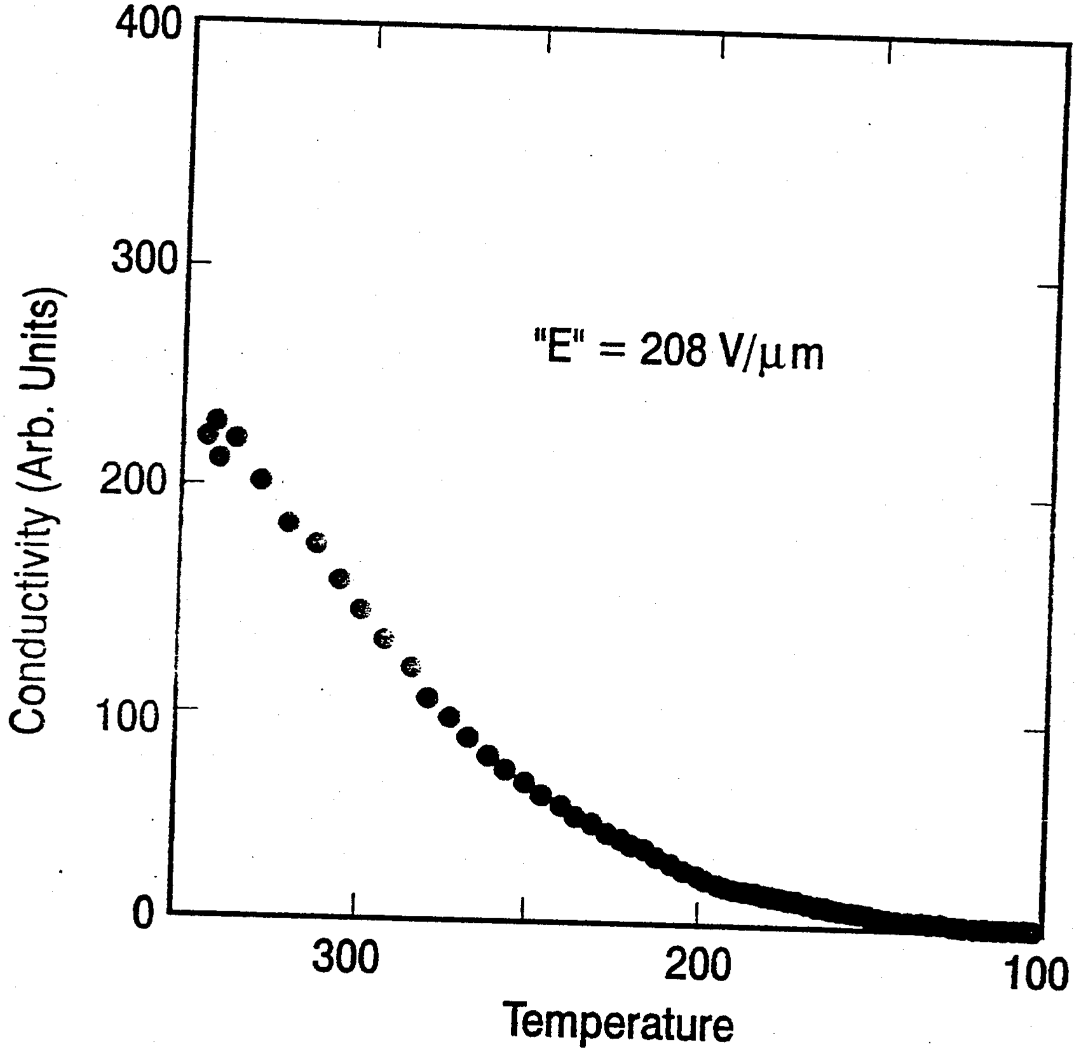


**Figure 14**. Conductivity of a **PI-6** film as a function of temperature (electric field = 208 V/$\mu$m).

Figure 15

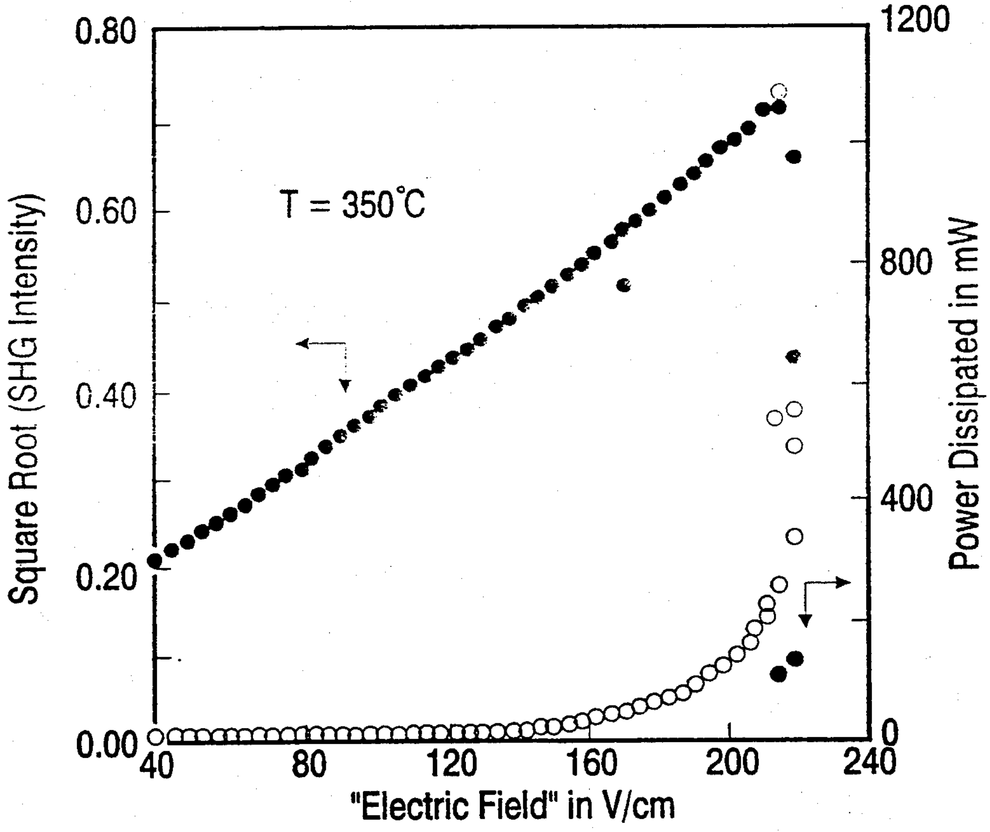


**Figure 15.** Second harmony intensity and power dissipated (**PI-6**) as a function of applied field at 350°C.

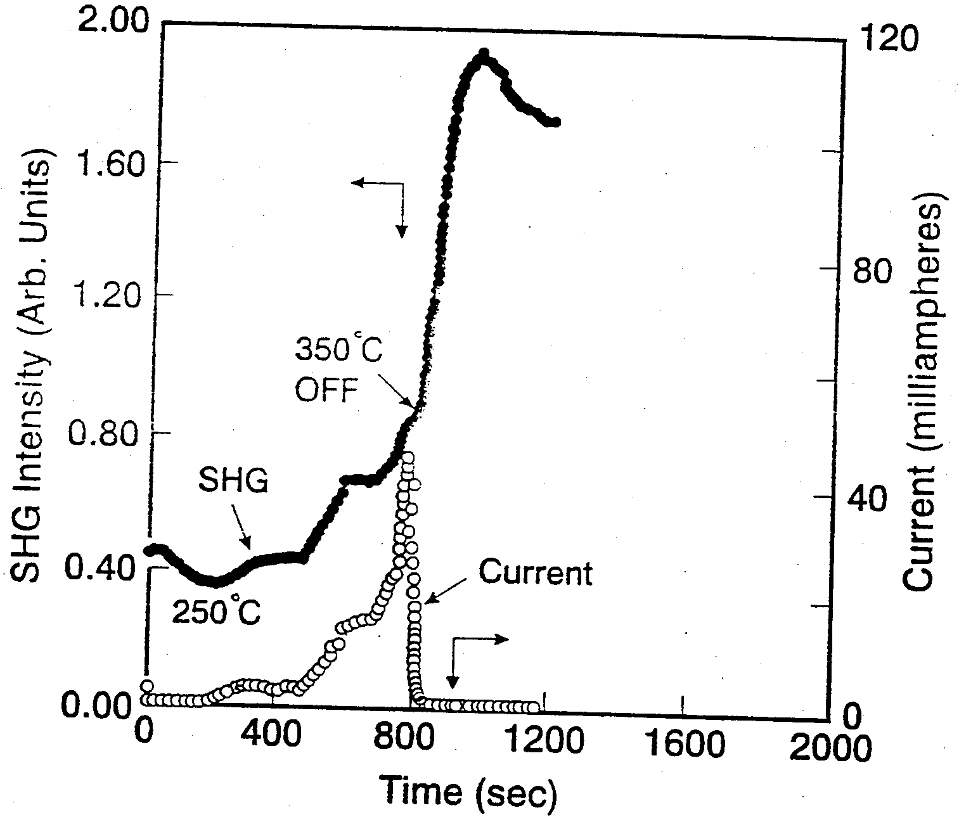


**Figure 16**. Plot of SHG and current for **PI-6** as a function of temperature ramping (8°C/minute). The heater was turned off at 350°C when the current began to increase rapidly.

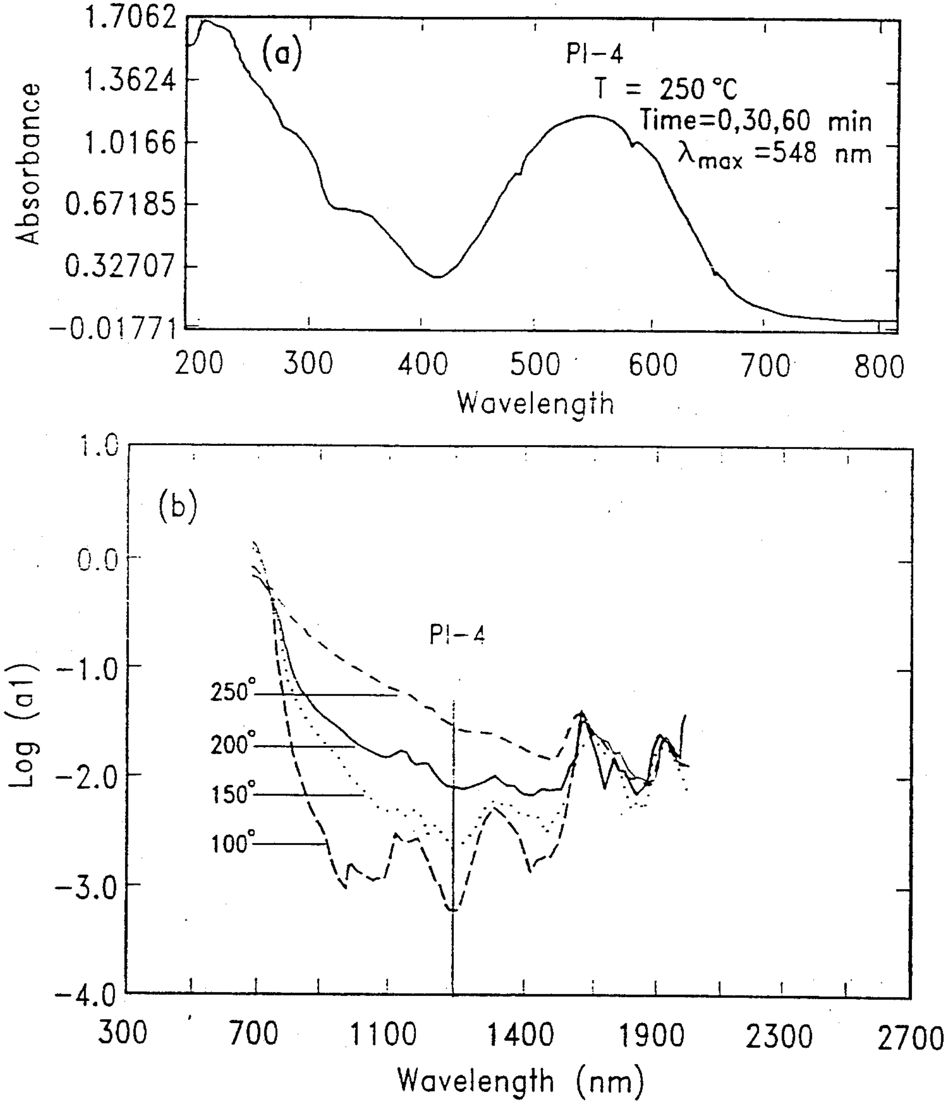


**Figure 17**. Optical losses upon heating **PI-4**: (a) Absorption spectra of **PI-4** after heating to 250°C; (b) PTD spectra of **PI-4** upon heating.

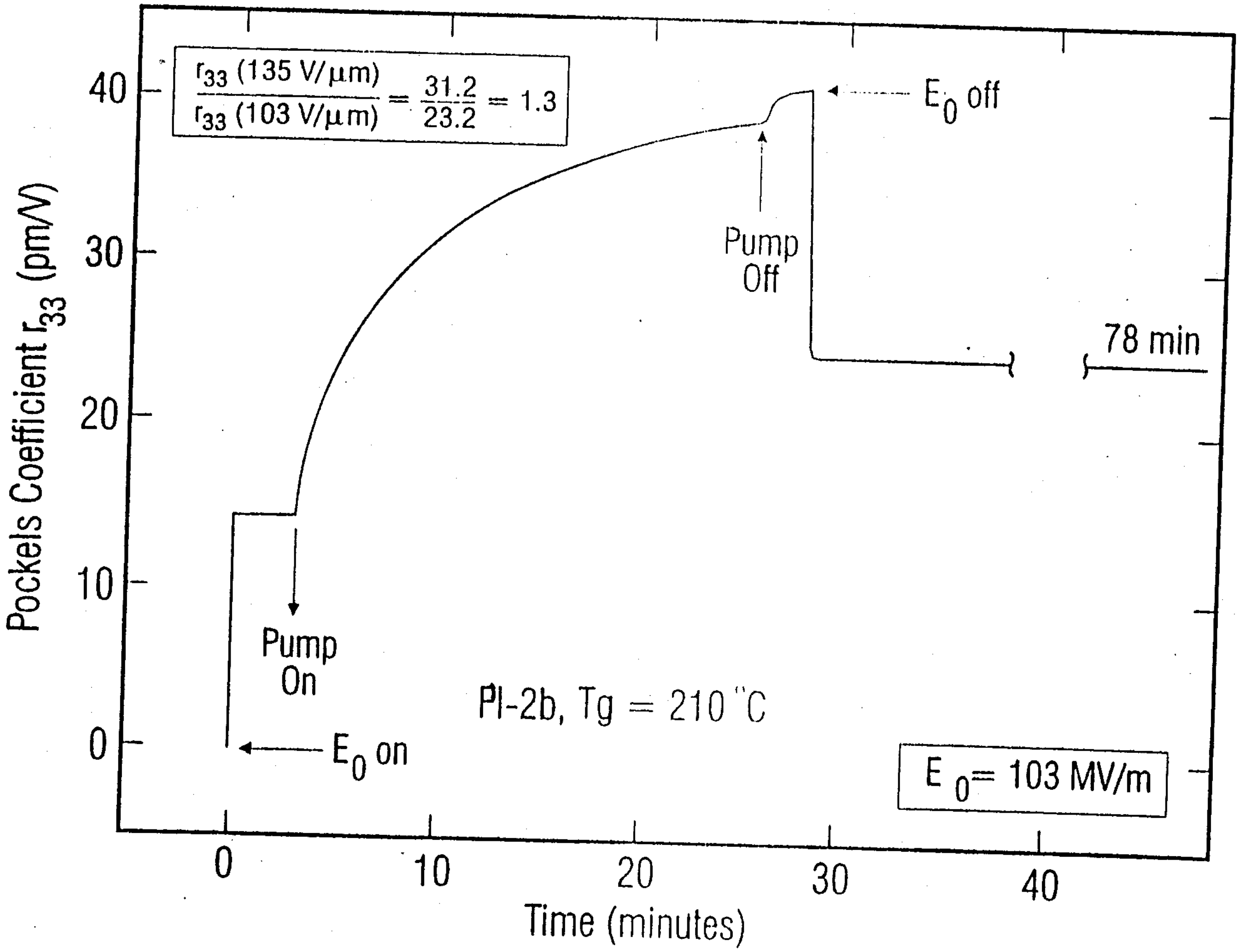


**Figure 18.** PEP profile of **PI-2b** pumped at 633 nm with circularly polarized light propagating perpendicular to the film surface. Poling field 103 MV/m, temperature 25°C.

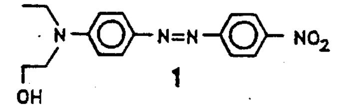
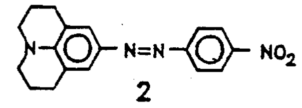
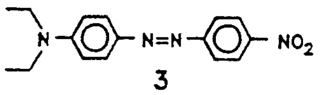
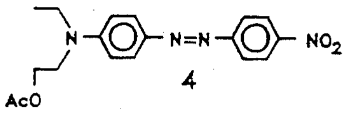
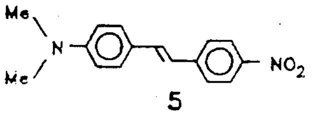
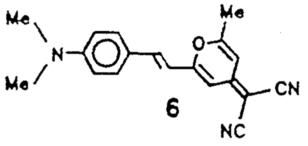
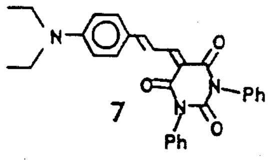
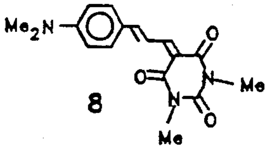
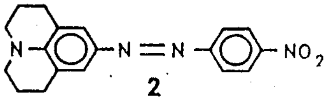
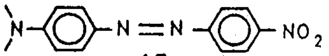
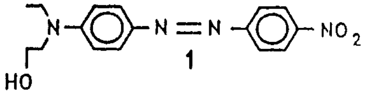
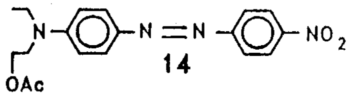
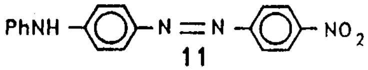
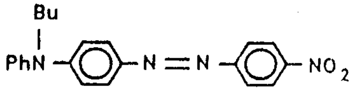
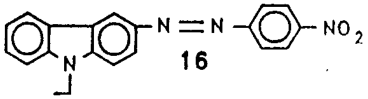
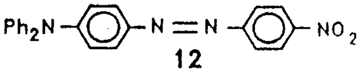
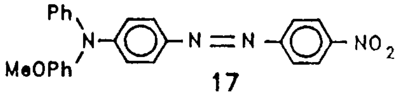
| Structure | $T_{mp}$ (°C) | $T_5$ (°C)$^a$ | $T_d$ (°C)$^b$ | $\Delta(T_d-T_m)$ (°C) | $T_d^{0\,c}$ (°C) |
|---|---|---|---|---|---|
|  1 | 169 | 258 | 309 | 140 | 255 |
|  2 | 190 | 240 | 242 | 52 | 182 |
|  3 | 156 | 245 | 322 | 166 | 270 |
|  4 | 130 | 272 | 330 | 200 | --- |
|  5 | 256 | 262 | 290 | 34 | 257 |
|  6 | 227 | 322 | 332 | 105 | 255 |
|  7 | 265 | 292 | 268 | 3 | --- |
|  8 | 254 | 322 | 277 | 23 | --- |

**Table I.** Thermal properties of some typical NLO chromophores. (a) Temperature at which 5% of the sample weight is lost as determined by TGA at a scanning rate of 20°/minute. (b) Decomposition onset temperature determined by DSC at a heating rate of 20°/minute. (c) Equilibrium onset decomposition temperature determined by the extrapolation of onset decomposition temperature versus heating rate curves to zero heating rate.

chromophores containing alkyl and/or arylamino donor substituents. (a) Measured at 20°/minute.

(b) Measured in $CHCl_3$ unless otherwise noted. (c) Measured in p-dioxane.

| Structure | mp (°C) | $T_d$ (°C)[a] | $\lambda_{max}$[b] (nm) |
|---|---|---|---|
|  **2** | 190 | 242 | 552 |
|  **13** | 238 | 307 | 480 |
|  **1** | 169 | 305 | 474[c] |
|  **14** | 130 | 330 | 472 |
|  **11** | 165 | 364 | 452 |
|  **15** | 163 | 340 | 484 |
|  **16** | 180 | 362 | 438 |
|  **12** | 151 | 393 | 486 |
|  **17** | 162 | 380 | 500 |

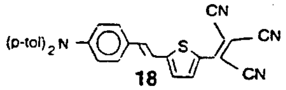
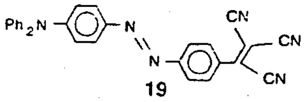
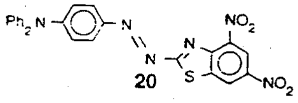
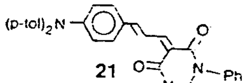
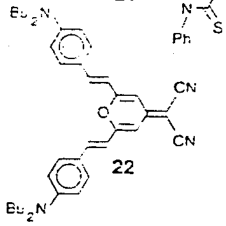
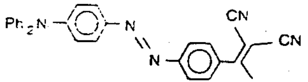
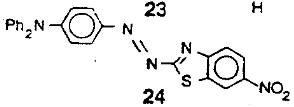
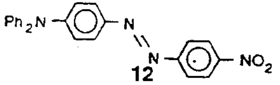
| Structure | $\lambda_{max}$ (nm) | $T_d$(°C) | $T_d^0$(°C) [a] | $\mu\beta^{EO}_{1300}$/MW x$10^{30}$ [b] | $r_{33}$ (calc) (pm/V) [c] |
|---|---|---|---|---|---|
|  18 | 680 | 331 | 263 | 14.1 | 85.0 |
|  19 | 602 | 364 | 250 | 6.2 | 37.0 |
|  20 | 594 | 324 | 275 | 5.3 | 32.0 |
|  21 | 594 | 320 | N/A | 3.7 | 22.0 |
|  22 | 496 | 348 | 295 | 3.7 | 22.0 |
|  23 | 526 | 383 | 312 | 3.2 | 19.0 |
|  24 | 550 | 356 | 292 | 3.1 | 18.5 |
|  12 | 498 | 393 | 352 | 2.0 | 12.0 |

**Table III**. Thermal and nonlinear properties of some thermally stable NLO chromophores. (a) Decomposition onset temperatures measured by DSC at a heating rate of 20°/minute. (b) Calculated reduced molecular nonlinearities at 1300 nm. (c) Estimated electro-optic coefficient at 1300 nm assuming a chromophore loading level of 50 wt.% in a polymer with optical and dielectric constants of commercially available ULTEM. A poling temperature of 250°C and a poling field of 250 V/$\mu$m were assumed in this calculation.[8,14,23]

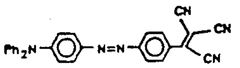
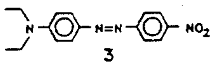
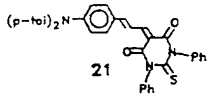
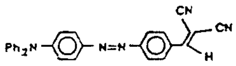
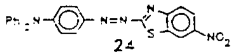
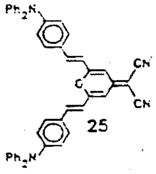
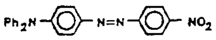
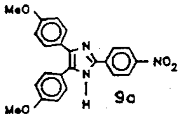
| Structure | $\beta_0 \times 10^{30}$ [a] (esu) | $\mu\beta^{E0}_{1300} \times 10^{30}$ [b] ($cm^5 \cdot D/esu$) | $T_d$ (°C) [c] | $T_d^*$ (°C) [d] | Thermal Decomposition | | |
|---|---|---|---|---|---|---|---|
| | | | | | Temp (°C) | $\Gamma/\Gamma_0$ [e] | UV (normalized) [f] |
|  19 | 402 | 2,780 (6.1) [g] | 384 | 249 | 250<br>275<br>300 | 1.00<br>0.71<br>0.07 | 1.00<br>0.77<br>0.15 |
|  3 | 147 | 1,000 (3.4) [g] | 322 | 270 | 225<br>250<br>300 | 1.00<br>0.95<br>--- | 0.99<br>0.85<br>--- |
|  21 | 357 | 2,220 (3.7) [g] | 320 | --- | 250<br>275 | 0.93<br>0.01 | 0.97<br>0.02 |
|  23 | 231 | 1,360 (3.2) [g] | 383 | 310 | 250<br>275<br>300 | 1.00<br>0.88<br>0.01 | 1.00<br>0.90<br>--- |
|  24 | 215.4 | 1,400 (3.1) [g] | 356 | 291 | 250<br>275<br>300 | 1.00<br>0.93<br>0.03 | 1.00<br>0.93<br>--- |
|  25 | 188.4 | 1,550 (2.3) [g] | 404 | 304 | 325<br>350<br>375 | 0.81<br>0.46<br>0.16 | 0.76<br>0.60<br>0.14 |
|  12 | 162 | 794 (2.0) [g] | 393 | 352 | 250<br>300<br>350 | 1.00<br>1.00<br>0.88 | 0.98<br>0.96<br>0.85 |
|  9a | 56.7 | 164 (0.4) [g] | 345 | 305 | 250<br>300 | 0.93<br>0.83 | 0.97<br>0.82 |

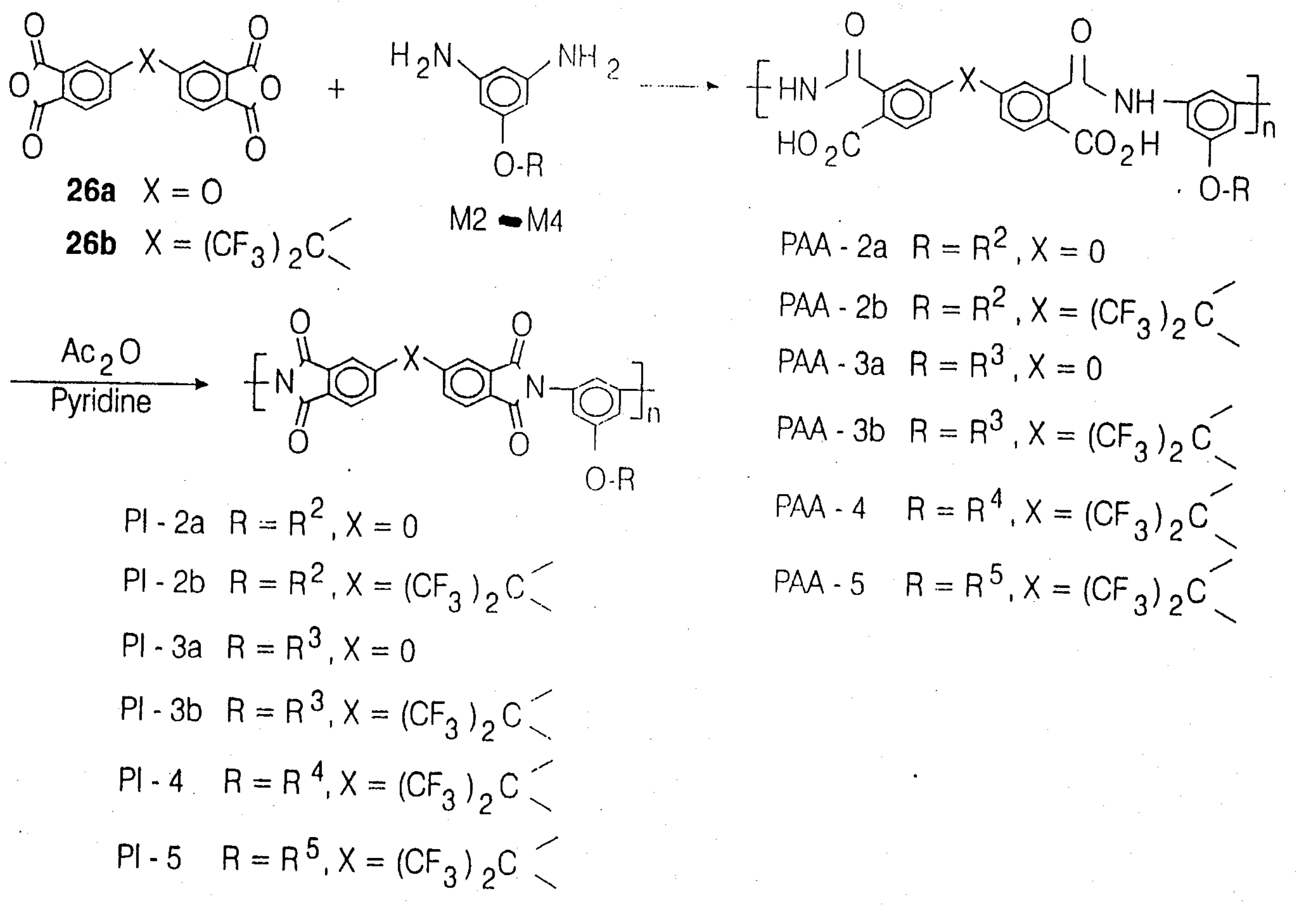
**Table IV**. Thermal and nonlinear properties of a variety of NLO chromophores. (a) Corrected molecular hyperpolarizability [$\beta(-2\omega;\omega,\omega)$] measured by EFISH extrapolated to zero frequency. (b) Poled electro-optic molecular nonlinearity extrapolated to 1300 nm. (c) Decomposition onset temperature measured by DSC at a heating rate of 20°/minute. (d) Extrapolated value of the decomposition onset temperature. (e) Normalized nonlinear susceptibility of samples heated to 30 minutes to temperature versus unheated samples as measured by EFISH in chloroform solution. (f) Normalized absorbance; i.e., solution absorbance in chloroform at the $\lambda_{max}$ of samples heated for 30 minutes and redissolved versus unheated samples. (g) Calculated reduced molecular nonlinearity at 1300 nm ($\mu\beta(-\omega;\omega,0)/MW$)).

| Chromophore | $T_d$ (°C) | $T_d^0$ (°C) | $T_{1/2}$ (10%)[a] EFISH (°C) | $T_{1/2}$ (10%)[b] UV-VIS (°C) | $T_{1/2}$ (10%)[c] DSC (°C) | $T_{1/2}$ (10%)[d] UV-VIS (Polyimide) |
|---|---|---|---|---|---|---|
| **3** | 322 | 270 | 242 | 254 | 251 | 263 |
| **12** | 393 | 352 | 342 | 328 | 312 | 325 |
| **19** | 364 | 249 | 257 | 260 | 227 | -- |
| **23** | 383 | 310 | 273 | 275 | 261 | -- |
| **24** | 356 | 291 | 276 | 276 | 254 | 282 |

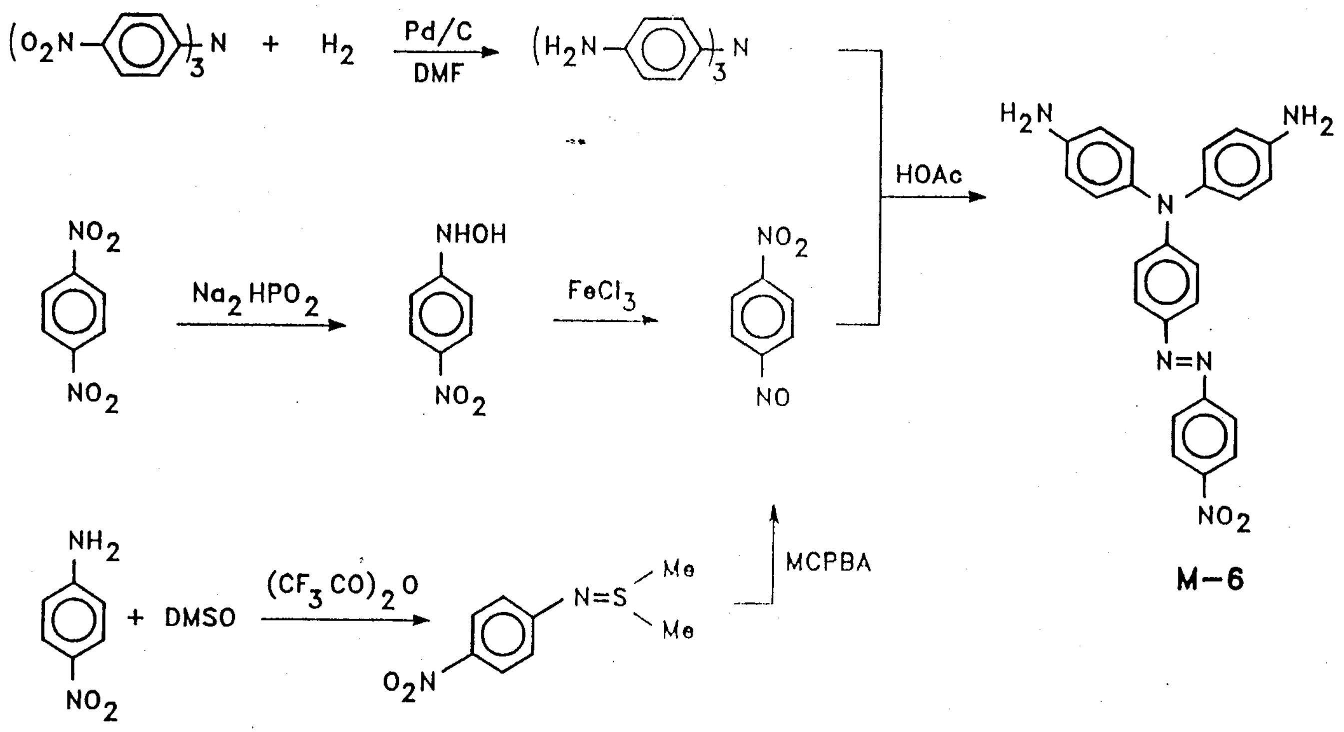
**Table V.** Thermal stability comparisons of a variety of NLO chromophores using the thermal protocol techniques. (a) Temperature for which 10% of the original chromophore nonlinearity is lost after 0.5h heating. (b) Temperature where 10% of the molar extinction coefficient at the original long wavelength $\lambda_{max}$ is lost after heating for 0.5h. (c) Temperature where 10% of the heat of the original exothermic DSC decomposition is lost after 0.5h heating. (d) Temperature where 10% of the original absorbance at the $\lambda_{max}$ is lost upon heating for 0.5h for chromophores tethered to a polyimide backbone.

| Polyimide | $T_{pol}$ [a] (°C) | $T_g$ [b] (°C) | $\lambda_{max}$ (nm) | Chromophore Wt. % | $r_{33}$ (1.3 $\mu$m) (pm/V) |
|---|---|---|---|---|---|
| PI–2b | 205 | 213 | 474 | 36 | 3.75 [c] |
| PI–3a | 210 | 223 | 500 | 47 | 8.2–10.0 [d] |
| PI–3b | 220 | 228 | 498 | 45 | 7.0 [e]<br>8.1 [f]<br>3.1 [c] |
| PI–4 | 220 | 225 | 548 | 53 | 2.45 [c] |
| PI–5 | 210 | 210 | 496 | 58 | 13.0 [g] |

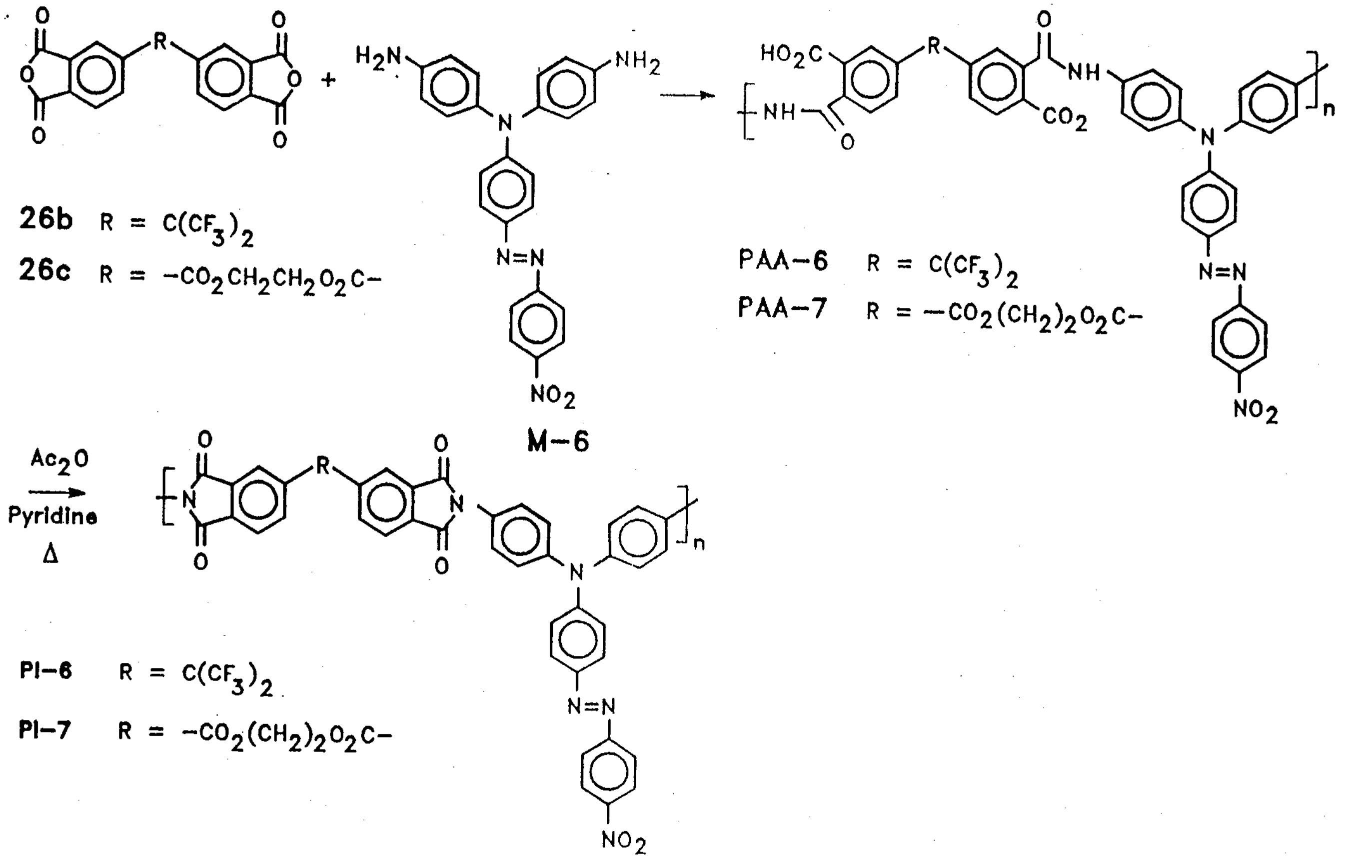
**Table VI**. The thermal, linear and nonlinear optical properties of a variety of NLO functionalized side chain polyimides: (a) poling temperature; (b) polymer glass transition temperature as measured by DSC analysis at a heating rate of 20 /minute; (c) electrode poling (75 V/$\mu$m), $r_{33}$ value measured by ellipsometry; (d) corona poling (~ 230 V/$\mu$m), $r_{33}$ measured at 1.3 $\mu$m by attenuated total reflection (ATR); (e) corona poling (~ 200 V/$\mu$m); (f) measured in a stacked three-level waveguide phase modulator; (g) corona poling (~ 230 V/$\mu$m), $r_{33}$ measured by ATR at



**Scheme 1.** Preparation of tethered NLO polyimides by condensation polymerization.



**Scheme 2.** The synthesis of the monomer M-6 used in the preparation of embedded donor type NLO polyimides.



**Scheme 3**. Preparation of embedded donor type NLO polyimides by condensation polymerization.