Orientational Relaxation in Electric-Field-Poled Films from Main-Chain Nonlinear Optical Polyamides

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ABSTRACT: The orientational relaxation of the NLO-phores in polyamides based on 2′,5′-diamino-4-(dimethylamino)-4′-nitrostilbene (DDANS) and linear aliphatic diacid chlorides was investigated at different temperatures below the glass transition by the decay of the nonlinear optical susceptibilities of corona-poled thin films. The time dependence of the decay was found to be well represented by the Kohlrausch–Williams–Watts stretched exponential function. The temperature dependence of the decay could be correlated with the glass transition temperature T_g using a normalized relaxation law with $(T_g - T)/T$ as the relevant scaling parameter. For one of the polyamides, showing a T_g of 176 °C, no decay of the NLO coefficient was observed at 25 °C within 8 months. For the purely orientational relaxation at 80 °C a relaxation time of significantly over 10 years could be estimated. As shown by UV–vis spectroscopy, the long-term stability of the new polyamides is restricted by the limited thermal stability of the NLO-phore. The polyamides investigated exhibit an enhanced orientational stability, as can be seen from the aging data. They represent a new approach to the design of polymers with large and stable second-order nonlinear optical properties, where the nonlinear optical units are fixed in the polymer backbone with their dipole moments oriented transversely to the main chain.

I. Introduction

In recent years there has been considerable interest in nonlinear optical (NLO) and electro-optic (EO) polymers because of their potential application in efficient, ultrafast, and low-voltage integrated electro-optical devices.[1] The frequently cited advantages of poled polymers are large nonlinear susceptibilities, fast response times, and easy processability. However, additional requirements such as long-term stability of the NLO or EO effect, high physical and mechanical stability, and low optical propagation losses must be satisfied before polymeric materials can demonstrate their potential as actual device materials.[1]

Insufficient stability of the induced noncentrosymmetric orientation of the NLO-phores at elevated temperatures, as expected for device processing (up to 250 °C) and operation (80 °C), is a major hindrance to further progress in developing polymeric NLO devices.[2] Different design strategies have been proposed for polymers with enhanced orientational stability of the NLO-phores. Generally, polymer systems with increased glass transition temperature show an improved orientational stability of the NLO-phores, although the efficacy varies depending on how the NLO-phore is incorporated into the polymer matrix. Covalent connection of the NLO-phore to the polymer is advantageous; typically, the NLO-phores have been attached as side chains to the polymer backbone.[3–5] Other approaches are based on cross-linked polymers[6,7] or polymers which incorporate the NLO-phores with their dipole moments head-to-tail in the main chain.[8,9]

Recently, we proposed a new approach to NLO polymers with large and stable second-order nonlinear susceptibilities where the NLO-phores are part of the polymer backbone and are linked with small spacer units.[10] The dipole moments of the NLO-phores are oriented transversely to the polymer main chain, a consequence of the assumption that in this arrangement the NLO-phores are easier to orient by an external field than in structures where their dipole moments are pointing along the polymer main chain. We have reported the preparation of a series of semiflexible polyamides based on the bifunctional NLO-phore 2′,5′-diamino-4-(dimethylamino)-4′-nitrostilbene (DDANS) and different linear aliphatic diacid chlorides (Figure 1). The polymers are amorphous, showing glass transition temperatures that depend on the number of methylene groups of the diacid chloride and range from 125 up to 206 °C. Transparent thin films of these polymers were oriented by a corona discharge poling process, and second-order nonlinear optical coefficients (d_{33}) of up to 40 pm/V at a fundamental wavelength of 1542 nm and electro-optical coefficients (r_{33}) of up to 16 pm/V (1300 nm) have been determined.[10] In the present paper the orientational relaxation of the NLO-phores in corona-poled films is investigated at different temperatures below the glass transition by the decay of the nonlinear optical susceptibilities of corona–poled thin films.

II. Results and Discussion

Samples. The polymers investigated in this work are poly{[2-[2-[4-(dimethylamino)phenyl]vinyl]-5-nitro-1,4-phenylene]iminocarbonyldodecamethylenecarbonylimino} (**P$_{12}$**) (T_g = 125 °C, x = 12 methylene units [see Figure 1]) and poly{[2-[2-[4-(dimethylamino)phenyl]vinyl]-5-nitro-1,4-phenylene]iminosuberoylimino] (**P$_6$**) (T_g = 176 °C, x = 6 methylene units [see Figure 1]). Synthesis and characterization of these polymers have been described previously, including detailed linear and nonlinear optical measurements.[10] Polymers **P$_{12}$** and **P$_6$** were chosen from the prepared series because these are the polymers with the lowest and the highest glass

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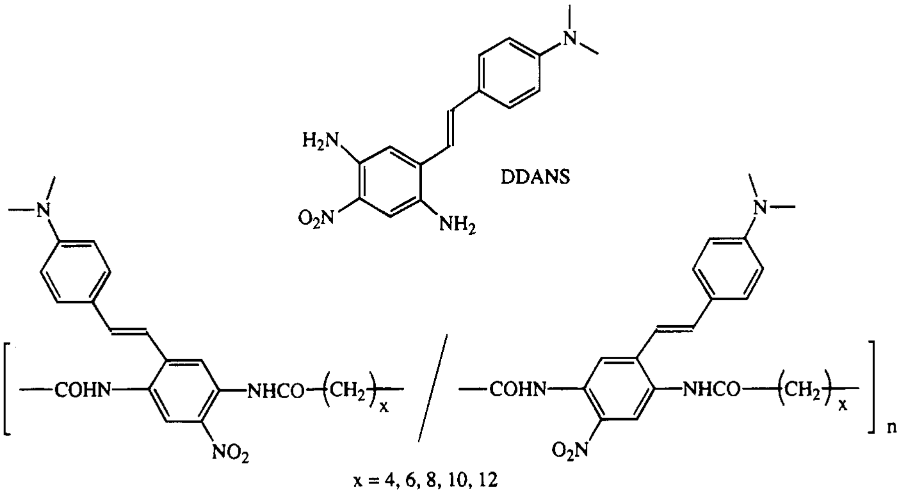

Figure 1. DDANS and the aromatic-aliphatic NLO polyamides.

transition temperatures of the prepared series (omitting a polymer with a T_g of 206 °C, in the range of thermal decomposition as determined by DSC). Both polymers could be processed into thin, dark-red and transparent films by spin coating from NMP solutions on heated substrates. The films were baked in a vacuum oven to remove all traces of residual solvent. Orientation in the films was induced by corona poling above T_g. This process was standardized to yield good and reproducible results for both polymers $\mathbf{P}_{12}$ and $\mathbf{P}_6$.

Thermal Stability. A critical characteristic of organic nonlinear optical materials that restricts device processing and device operation temperatures is the generally limited thermal stability of the highly polar NLO-phores.[11,12] The thermal behavior of polymers $\mathbf{P}_{12}$ and $\mathbf{P}_6$ has already been investigated using DSC and TGA analysis.[10] The first decomposition step that was attributed to the decomposition of the NLO-phores sets in at around 210 °C and shows a maximum decomposition rate at 300 °C in air and also under nitrogen atmosphere. Although DSC and TGA experiments have frequently been used to prove the stability of NLO-phores,[11,12] a more specific statement concerning the behavior of the active NLO-phores can be made by the time- and temperature-resolved analysis of the NLO-phores's charge-transfer absorptions using UV–vis spectroscopy. This technique was used in the present work, in order to check whether thermal degradation effects influenced the optical properties of polymers $\mathbf{P}_{12}$ and $\mathbf{P}_6$ during orientational relaxation experiments at elevated temperatures.

Exemplary thermal stability experiments are reported here for polymer $\mathbf{P}_{12}$. The absorption of the NLO-phore's charge-transfer absorption band (at 470 nm) in thin vacuum-dried films on fused silica was compared to that of the untreated ("original film") samples after different intervals of thermal aging at temperatures between 80 and 185 °C. The results are summarized in Figure 2. Even at temperatures much lower than the decomposition temperatures determined by DSC and TGA, a decrease of the NLO-phore concentration due to thermal degradation was found. These results have to be taken into account for the relaxation experiments.

Orientational Stability. The orientational relaxation of the NLO-phores was investigated at different temperatures below the glass transition by the decay of the nonlinear optical susceptibilities $\boldsymbol{d}$ (measured as d_{33}) of corona-poled thin films of polymers $\mathbf{P}_{12}$ and $\mathbf{P}_6$ using a standard Maker fringe technique[13] at a fundamental wavelength of 1338 nm. The reliable description of the relaxation process requires an accurate determination of the initial NLO coefficient $\boldsymbol{d}_0$ and the investigation of the decay of the NLO coefficient $\boldsymbol{d}(t)$ in a wide temperature and time range.[14] Therefore two different procedures have been applied for two different regimes of time and temperature.

For short time relaxation experiments at temperatures of 107 or 116 °C ($\mathbf{P}_{12}$) and 158 or 167 °C ($\mathbf{P}_6$), the samples were stored after poling for at least 1 day at room temperature in the absence of electric fields to ensure that any residual surface charges from the poling process that might stabilize the noncentrosymmetric orientation[15] had been dissipated. After this time, the initial NLO susceptibility $\boldsymbol{d}_0$ was measured at room temperature. The sample was then rapidly heated to the desired temperature, and the decay of the NLO susceptibility $\boldsymbol{d}(t)$ was continuously monitored.

For long-time relaxation experiments at 25 or 80 °C ($\mathbf{P}_{12}$ and $\mathbf{P}_6$), samples were stabilized at the desired temperature at the end of the poling process in the presence of the poling field. When the poling field was switched off, a fast and significant decay of the SHG signal was observed (Figure 3). This decay was attributed to the disappearance of the $\chi^{(3)}(-2\omega;\omega,\omega,0)$ contribution to the signal which is analogous to the effect used in EFISH (electric-field-induced second harmonic generation) and originates from the interaction of the optical signal with the strong electrical poling field.[16] Therefore the relaxation measurement was started only 60 s after switching off the poling field, and the value then measured was taken as the initial NLO susceptibility $\boldsymbol{d}_0$. The NLO susceptibility $\boldsymbol{d}(t)$ was then continuously monitored for up to 60 min. After this time, the samples were stored further at the desired temperature and the NLO coefficients were measured in intervals over up to 8 months.

In most cases the time dependence of the measured decays of the nonlinear optical susceptibility was found to be well represented by the Kohlrausch–Williams–Watts (KWW) stretched exponential function, often used to characterize the orientational relaxation of NLO-phores in polymers:[14,17]

$$\boldsymbol{d}(t) = \boldsymbol{d}_0 \exp[-(t/\tau)^{\beta}] \qquad (1)$$

where τ is the characteristic relaxation time that is

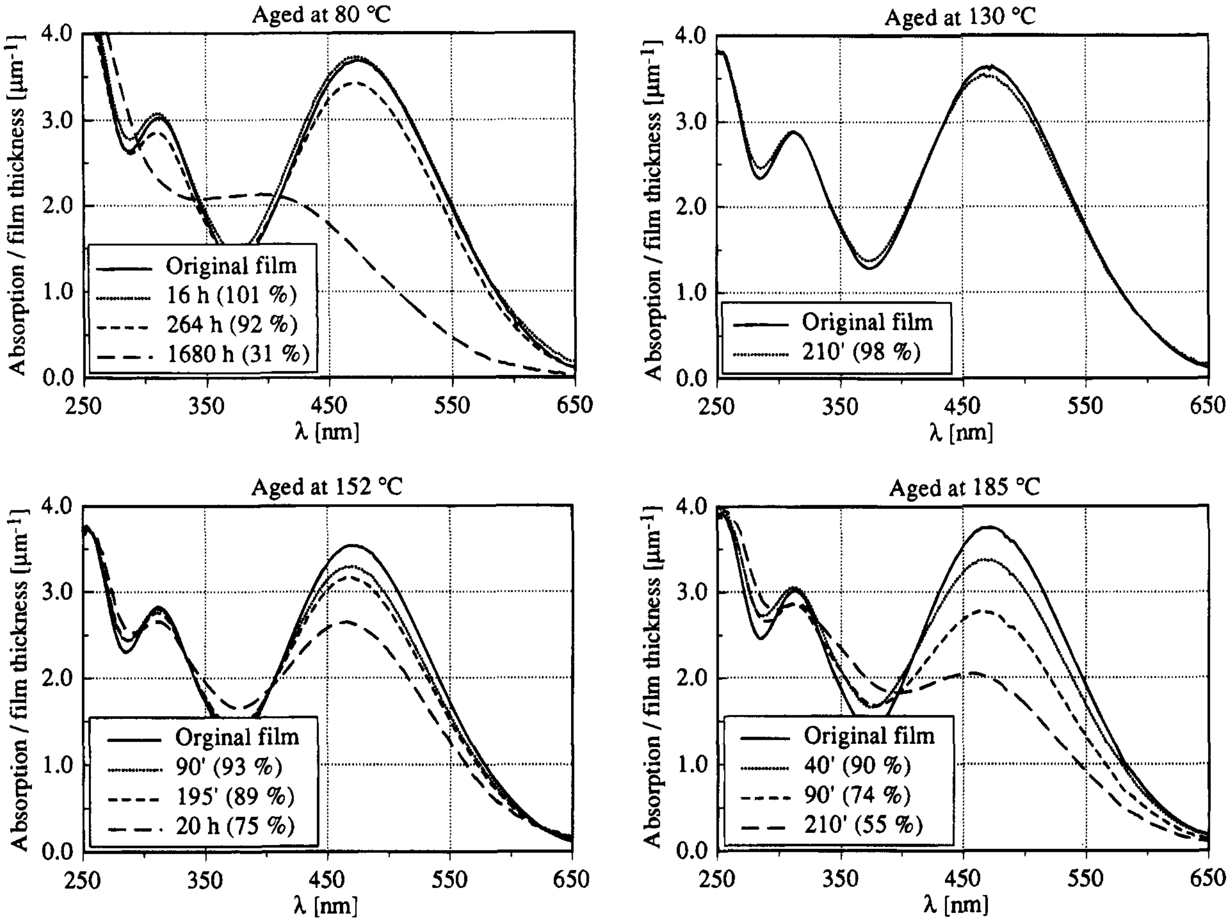

Figure 2. Thermal stability of thin films of polymer $\mathbf{P}_{12}$. The absorption was measured after different intervals of thermal aging at 80, 130, 152, and 185 °C. Values in parentheses are the maxima of the NLO-phore's charge-transfer bands relative to the untreated ("original film") samples.

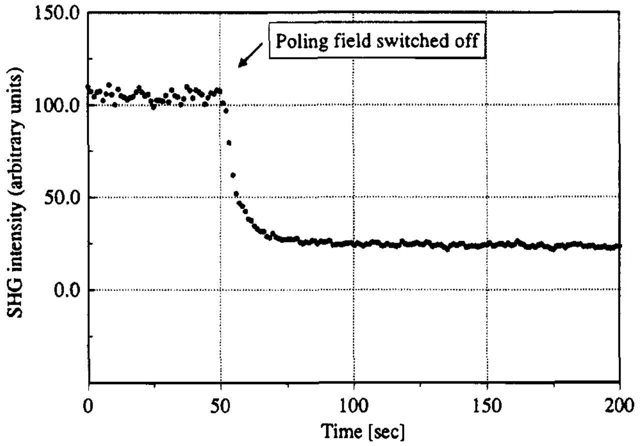

Figure 3. SHG signal of a poled film of polymer $\mathbf{P}_6$ at 80 °C after switching off the poling field. The fast initial decay was attributed to the disappearance of the third-order frequency-doubling effect originating in the interaction of the optical signal with the electrical poling field.

required for the NLO susceptibility $\boldsymbol{d}(t)$ to decay to 1/e of its initial value $\boldsymbol{d}_0$. The function represents in its original sense a continuous distribution of single exponential decays where $0 < \beta \leq 1$ is a measure of the breadth of the distribution and the extent of deviation from single exponential behavior. We emphasize that in the present study the decay of the nonlinear optical susceptibilities cannot be attributed to a single mechanism because there is evidence for some chemical degradation in addition to the orientational relaxation (see above). However the KWW function was found suitable to describe the decay of the nonlinear optical susceptibilities, especially in the longer time portion of the decay.

Figure 4 shows the measured decay of d_{33} for polymer $\mathbf{P}_6$ at four different decay temperatures in a semilogarithmic plot. The stretched exponential functions have been fitted using the experimental value for $\boldsymbol{d}_0$. The results are summarized for polymers $\mathbf{P}_{12}$ and $\mathbf{P}_6$ in Table 1. Before the relaxation data are interpreted, they have to be compared with the results from thermal stability experiments. At higher temperatures (107 and 116 °C in the case of $\mathbf{P}_{12}$, 158 and 167 °C in the case of $\mathbf{P}_6$) the thermal degradation is negligible compared to the orientational relaxation of the NLO-phores as mechanism of the decay of the nonlinear optical susceptibility; this decay is assumed to originate mainly from orientational relaxation processes. At 25 °C both processes, thermal degradation and orientational relaxation, are very slow, resulting in a barely detectable decay of the NLO susceptibility, and therefore no statement can be made about which process is the limiting factor.

At 80 °C the thermal degradation is an important process. While the UV–vis absorption of the NLO-phore's charge-transfer band decays in 10^6 s to about 92% of its original value, the NLO susceptibility decreases in this time to about 40% in the case of $\mathbf{P}_{12}$ and about 85% in the case of $\mathbf{P}_6$. The time in which the UV–vis absorption decays to 30% (6×10^6 s) is of the same order of magnitude as the determined relaxation time τ. Hence we conclude that thermal decomposition is neither neglectable nor dominant in case of polymer $\mathbf{P}_{12}$

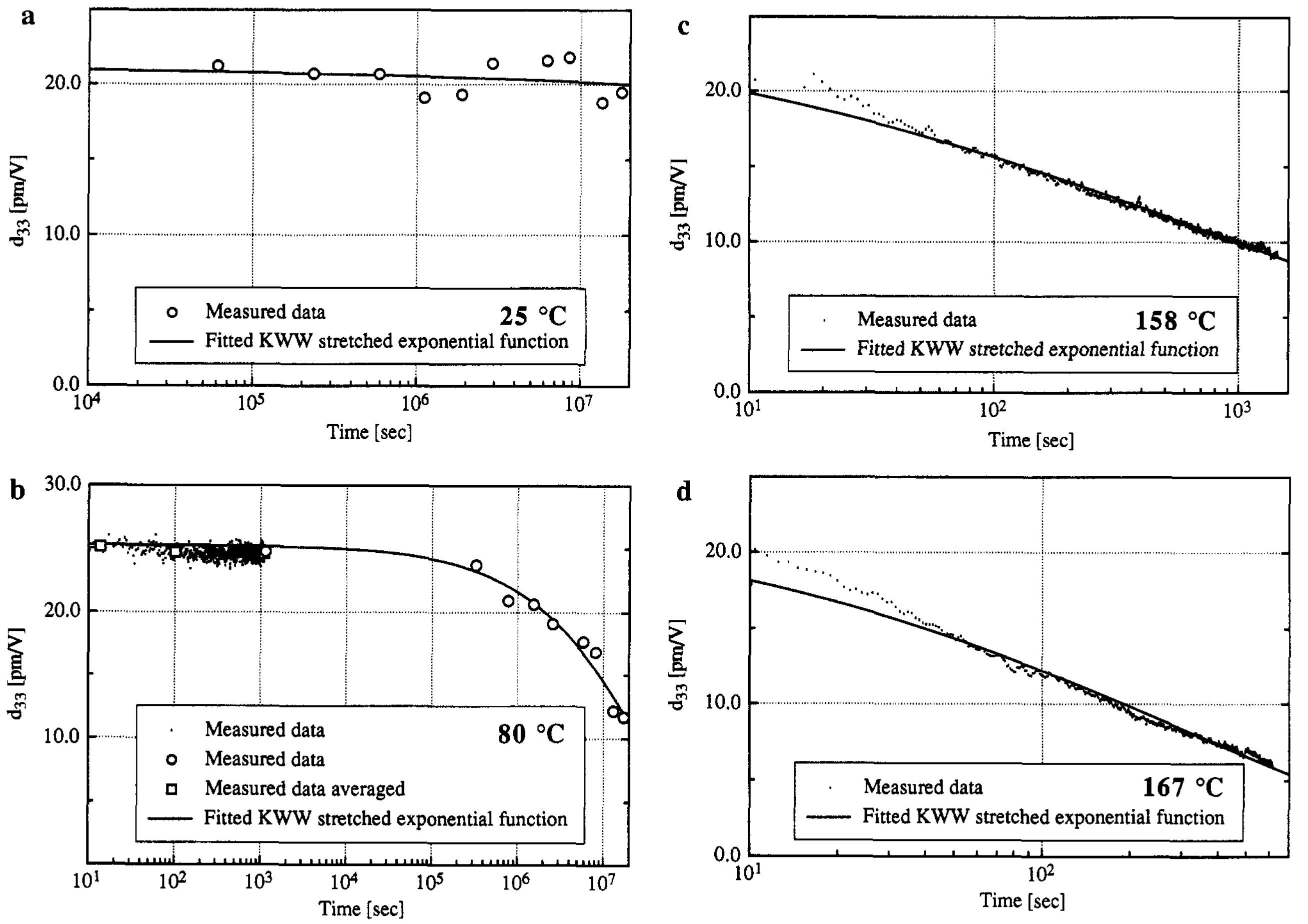

Figure 4. SHG relaxation of thin films of polymer P_6 as a function of time and temperature, determined at 25 (a), 80 (b), 158 (c), and 167 (d) °C.

Table 1. Results of the Relaxation Experiments at Different Temperatures

Polymer P_{12}

	25 °C	80 °C	107 °C	116 °C
d_0, pm/V	19	23	36	34
τ, s	2.3×10^{13}	1.7×10^6	1.3×10^4	560
β	0.15	0.27	0.31	0.47

Polymer P_6

	25 °C	80 °C	158 °C	167 °C
d_0, pm/V	21	25	26	23
τ, s	3.2×10^{13}	3.0×10^7 [a]	1140	290
β	0.20	0.55[a]	0.27	0.42

[a] Thermal degradation processes overlap the relaxation process significantly in this case; see text for details.

but plays the major role in the case of polymer P_6 in the decay of the NLO susceptibility.

The relaxation times τ range from a few minutes (at elevated temperatures) to the order of 10^6 years (at room temperature). The relaxation times determined at low temperatures are subject to some uncertainty since the measuring interval of 8 months is short compared to the extrapolated relaxation times. The values for β increase with temperature and range from 0.15 to 0.47. As expected, a significantly slower relaxation was observed for polymer P_6 than for P_{12} due to its higher glass transition temperature.

In order to compare the orientation–relaxation behavior of polymers with differing glass transition temperatures T_g, several relations between T_g, the temperature T, and the relaxation time τ have been proposed that are related to the Williams–Landel–Ferry or the Vogel–Tamann–Fulcher relation.[14,17–20] Here we employ the scaling relation proposed before,[14]

$$\tau(T) = A' \exp\left(\frac{T_g - T}{T}\right) \qquad (2)$$

where A' is a constant. Two types of processes have been found to be relevant for the decrease of the decay of NLO activity in our samples: thermal decomposition and orientational relaxation. When focusing on orientational relaxation only, we, therefore, omit from consideration all data points found to be significantly influenced by thermal decomposition (see above). The results of the relaxation experiments on polymers P_{12} and P_6 using this scaling relation are plotted in Figure 5. For purposes of comparison, the results of similar experiments[17,18] on guest–host systems (Lophine dye doped in a polyimide matrix, T_g = 170 and 190 °C) and of some of us[14] on side-chain polymers (Disperse red 1 attached to a polyimide main chain, T_g = 130 and 172 °C) are also included. As can be seen from Figure 5, the relaxation time of the new NLO polyamides appears to be linearly dependent on $(T_g - T)/T$ in the temperature range from T_g − 100 °C to T_g (although the precision of the data does not warrant a mechanistic conclusion). The experiment made at 25 °C on polymer P_6 shows a strong deviation from this linear relationship, comparable to the trend observed for side-chain polymers at temperatures below T_g − 50 °C.[18] Only a few data points are available at the moment, and the relaxation times determined at low temperatures are subject to some uncertainty due to errors in the ex-

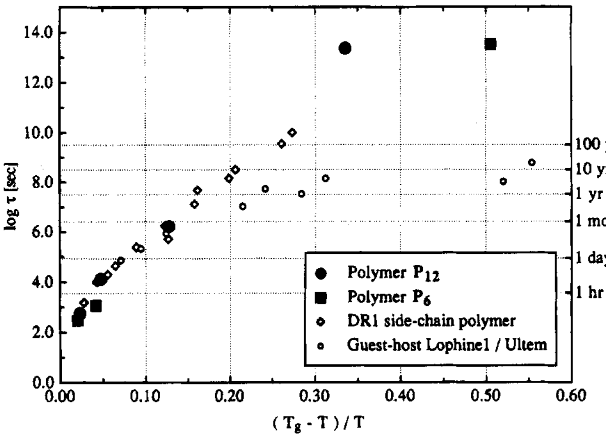

Figure 5. Scaling of relaxation times with $(T_g - T)/T$. DR1: Disperse red 1 attached to polyimide chain.[14] Lophine 1/Ultem: Lophine dye admixed to polyimid matrix.[17,18]

trapolation; hence, a conclusive interpretation of this behavior is not possible at the moment.

The new polyamides investigated here clearly show enhanced orientational stability of the NLO-phores, at least when compared to guest–host systems with comparable glass transition temperatures. No significant decay of the nonlinear optical susceptibilities could be detected for both polymers at 25 °C within 8 months. For the pure orientational relaxation of polymer $\mathbf{P_6}$ (the T_g of which is 176 °C) at 80 °C, a relaxation time of significantly over 10 years could be extrapolated.

III. Conclusions

We recently proposed a new approach to the design of NLO polymers with large second-order nonlinear susceptibilities where the NLO-phores are part of the polymer backbone with their dipole moments oriented transversely to the polymer main chain. These materials had been prepared with the aim of improved stability of the NLO characteristics. Now we present measurements concerning the long-term stability of the nonlinear optical susceptibility in these main-chain polyamides with glass transition temperatures up to 176 °C.

Thermal aging experiments showed that the time- and temperature-resolved spectroscopic analysis of the NLO-phore's charge-transfer absorption is to be preferred over DSC or TGA techniques. Even at temperatures significantly lower than the decomposition temperatures determined by DSC and TGA, a significant decomposition of the NLO-phore concentration could be proved. This thermal decomposition process was found to be a limiting factor for the long-term behavior of the nonlinear optical susceptibility of the high-T_g polyamide investigated. The NLO-phore used in our polymers, being based on DANS, is very similar to many commonly employed NLO-phores; hence, we suggest that the role of thermal stability of NLO-phores receives special attention.

The orientational relaxation of the NLO-phores was investigated at different temperatures below the glass transition by the decay of the nonlinear optical susceptibilities of corona-poled thin films. The time dependence of the decay was found to be well represented by the KWW stretched-exponential function.

The polyamides investigated in this work show a remarkable orientational stability of the NLO-phores when compared to guest–host systems with comparable glass transition temperatures. We surmise that the outstanding orientational properties of the new polyamides are predominantly based on the location of the NLO-phores in the skeletal structure of the backbone; this arrangement provides sufficient mobility for the orientation process but minimizes the orientational relaxation.

IV. Experimental Section

Materials. The polymers investigated here are poly{[2-[2-[4-(dimethylamino)phenyl]vinyl]-5-nitro-1,4-phenylene]iminocarbonyldodecamethylenecarbonylimino} ($\mathbf{P_{12}}$, T_g = 125 °C, x = 12 methylene units [see Figure 1]) and poly{[2-[2-[4-(dimethylamino)phenyl]vinyl]-5-nitro-1,4-phenylene]iminosuberoylimino} ($\mathbf{P_6}$, T_g = 176 °C, x = 6 methylene units [see Figure 1]). Synthesis and characterization of these polymers have been described previously, including detailed linear and nonlinear optical measurements.[10]

Film Preparation. The polymers were dissolved in dry NMP at concentrations of 4–8% w/w polymer. The solutions were filtered through a 0.45 μm filter and were spin-cast under heating either on substrates of fused silica (for UV–vis measurements) or on indium–tin oxide (ITO) glass (for nonlinear optical measurements). The polymer films were dried at 70 °C in vacuum for at least 24 h. The thickness of the films ranged from 0.2 to 0.7 μm, as measured with a Tencor Instruments Alpha-Step 2000 Profilometer.

Corona Poling. Films of $\mathbf{P_{12}}$ and $\mathbf{P_6}$ were corona poled with a dc electric field using glass substrates coated with a 20 nm thick ITO conductive layer (Balzers Baltracon 217) as the ground electrode and a tungsten corona needle. The applied corona voltage was + 13 kV at a poling current of <0.1 mA. The gap distance was approximately 3 cm. The films were heated on a custom made hotstage under applied field to 5–15 °C above T_g. They were held at this temperature for about 20 min and then cooled to room temperature or the desired relaxation temperature in the presence of the field at an average rate of 1.5–3 °C/min.

Thermal Treatment. The samples used for long-time aging experiments were stored under air in the dark at 25-(±3) or 80(±2) °C. The thermal aging of films at temperatures in the range 107–185 °C was conducted under air on custom made hot stages that allowed us to maintain the temperature to within ±2 °C.

Optical Measurements. UV–vis spectra of unpoled films were recorded on a HP 8452A diode array spectrophotometer.

Nonlinear optical measurements were performed using a standard Maker-fringe technique.[13] The experimental setup is shown in Figure 6. A BMI DNS 501 Q-switched Nd:YAG laser with a pulse width of 60 ns at a 30 Hz repetition rate and a pulse energy of ca. 10 mJ provided the fundamental wavelength of λ = 1338 nm. The polarization was chosen to be in the plane of incidence (parallel polarization). SHG coefficients have always been measured after switching off the poling field. Two different procedures have been applied.

For relaxation measurements in the range 107–167 °C the samples were stored after poling for at least 1 day at room temperature in the absence of any electric field. After this time, the initial NLO coefficient $\boldsymbol{d}_0$ was measured at room temperature by the rotation of the polymer film perpendicular to the incoming laser beam. The setup's hot stage was then heated to and stabilized at the desired temperature without the sample and the sample was then placed back on the hot stage. After the sample had reached the desired temperature (about 10–20 s), the decay of the NLO coefficient $\boldsymbol{d}(t)$ was continuously monitored by the measurement at a fixed angle of incidence of the laser beam with respect to the sample (ϕ = 25 or 30°).

For relaxation measurements at 25 or 80 °C, the samples were stabilized at the desired temperature at the end of the poling process in the presence of the poling field. About 60 s after the poling field was switched off, the decay of the SHG signal that is attributed to the disappearance of the above mentioned $\chi^{(3)}$ effect was completed. Therefore the relaxation measurement was started only 60 s after switching off of the poling field. The NLO coefficient $\boldsymbol{d}(t)$ was continuously monitored at a fixed angle of incidence of 25 or 30° for up to

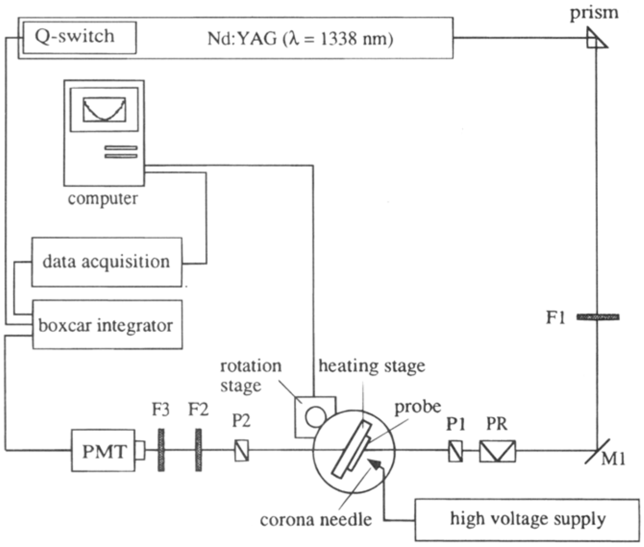

Figure 6. Experimental setup for SHG measurements. Filter F1 eliminates residual flashlamp light. PR: polarization rotator; P1, P2: polarizers. Filter F2 blocks the fundamental wave ($\lambda = 1338$ nm) and filter F3 attenuates the second harmonic signal. The intensity of the second harmonic signal is detected by a photon multiplier (PMT), averaged by a boxcar integrator, and recorded by a PC.

60 min. After this time, the samples were stored further at the desired temperature and the NLO coefficients were measured at regular intervals by the rotation of the polymer film perpendicular to the laser beam.

The measured SHG signals from the polymer films were calibrated with respect to the SHG signal of a quartz reference crystal ($d_{11} = 0.4$ pm/V).[21] The nonlinear optical coefficients d_{33} were evaluated as previously described.[10]

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