Second-Harmonic Response and Relaxation Behavior of High Glass-Transition Temperature Polyphosphazene Films

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Received March 13, 2000. Revised Manuscript Received August 25, 2000

The second-harmonic response of 4-[(4′-nitrophenyl)azo]phenoxy- doped polyphosphazene (PPZ) films with high glass-transition temperatures ($T_g \sim 150$ °C) has been investigated. The nonlinear chromophore has been incorporated into the PPZ as (i) a guest molecule (system I), (ii) a side-chain group covalently attached to the linear PPZ (system **II**), and (iii) a substituted group attached to a triphosphazene molecule that is dissolved in the PPZ (system **III**). The three components $\chi_{15}^{(2)}$, $\chi_{31}^{(2)}$, and $\chi_{33}^{(2)}$ of the second-order nonlinear optical susceptibility tensor have been determined for the three systems. Values for $\chi_{33}^{(2)}$ are in the range $5-15 \times 10^{-9}$ esu (∼1.7−6.0 pm/V), which appears significant and comparable to that found, under nonresonant conditions, in other polyphosphazene−chromophore systems with a much lower T_g. For equal chromophore concentration the guest−host system **I** shows the highest response. This has been correlated with a higher degree of molecular ordering achieved during poling. At variance with previous work, the SHG response of our three PPZ systems is very stable and has been comparatively investigated for various temperatures in the range room temperature−120 °C, always below T_g. At low enough temperatures (<100 °C) substantial differences are found between the three systems. The guest−host system **I** containing the free chromophore shows the fastest decay, whereas the one containing the triphosphazene molecule (system **III**) is the slowest. At 120 °C all systems present essentially the same behavior. The kinetics of the relaxation has been satisfactorily fitted to both the biexponential and KWW laws, and the values of the parameters have been discussed in light of previous results reported on other NLO organic polymers.

1. Introduction

Organic polymer materials are being increasingly considered for photonics applications.[1−6] They have a number of potential advantages over single crystals, both organic and inorganic, owing to their superior chemical flexibility, processability, and low cost. Polyphosphazenes (PPZ) are inorganic-backbone polymers[7−9] resulting from the repetition of the −P═N− monomer unit and appear as an interesting alternative to organic polymers. They present a number of useful features for practical devices. First, controlled incorporation of covalently linked chromophores can be easily accomplished over a broad concentration range. Consequently, most physical properties (mechanical, optical, ...) can be tailored by changing the nature and concentration of the side groups attached to the polymer chain by suitable molecular engineering. Moreover, by using polar side groups significant second-order nonlinear optical (SHG) responses have been achieved suggesting a promising potential for applications.[10] So far the NLO studies on PPZ are still very scarce, and the potential for nonlinear optical (NLO) applications remains mostly unexplored. In this perspective, they present an additional useful feature that is a wide transparence window permitting high transmission for both IR fundamental light and visible harmonic light. Unfortunately, reported glass-transition temperatures for PPZ are quite low (<100 °C) so that the electrooptic and SHG

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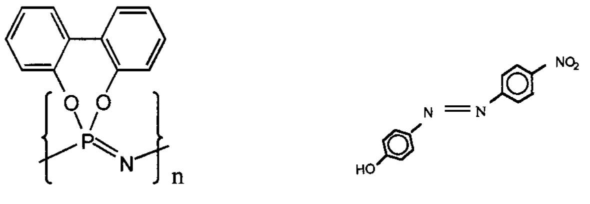
10.1021/cm001038d CCC: $19.00



PPZ (**1**) chromophore (**2**)

Figure 1. Chemical structures of the undoped polyphosphazene (1) and the NLO chromophore (**2**).

responses of the polymers become rapidly degradated.[10] However, for some applications this is not a problem. In particular, polyphosphazenes containing photoconducting and NLO side chains have been already synthesized and are good candidates for photorefractive devices.[11]

Recently, a new synthetic route has been developed[12,13] for the preparation of highly soluble and rigid polyphosphazenes with high glass-transition temperatures ($T_g > 150$ °C). This opens the way to obtain highly stable molecular ordering after electric-field poling and so achieve largely undegraded second-order nonlinear (particularly, electrooptic) susceptibilities. The purpose of this work has been to explore and ascertain the possibilities of these high T_g PPZ systems for second-order NLO devices and compare them with those achieved for previous PPZ with a lower T_g. Moreover, the performance of these novel PPZ will be also discussed in relation to that of organic polymers that have been more extensively studied. To that end, poly(2,2′-dioxybiphenyl)phosphazene (PPZ **1**), illustrated in Figure 1a, was synthesized by following the procedure previously reported.[12,13] The 2,2′-dioxybiphenyl group facilitates the synthesis, gives stability to the polymer chain, and yields high T_g values. To induce SHG activity the group 4-[(4′-nitrophenyl)azo]phenoxy (chromophore 2), Figure 1b, has been incorporated into the polymer. It is essentially similar to the well-known DO3 (dispersed orange)[14] NLO chromophore, except for the substitution of the OH end instead of the NH_2 one. A similar chromophore has been already used as NLO dopant in several PPZ polymers with a low T_g so that a meaningful comparison can be made. As shown in Figure 2, three strategies have been followed for the incorporation of the chromophore: (i) dissolved in the PPZ as a guest molecular group (system I), (ii) covalently attached as a side group to the linear PPZ main chain (system **II**), and (iii) as a substituted group to a triphosphazene molecule that is then dissolved in the PPZ polymer (system **III**). In the three cases the films have been prepared by spin-coating on glass substrates and then subsequently poled through a corona discharge technique.[15] To provide information on the degree of ordering induced by the poling for the three systems, the effect of the poling field on the optical absorption spectra has been determined. This is key information to make a meaningful comparison between the SHG response of different polymers that is not often provided. The three nonzero components $\chi_{15}^{(2)}$, $\chi_{31}^{(2)}$, and $\chi_{33}^{(2)}$ of the second-order nonlinear optical susceptibility tensor corresponding to $C_{\infty v}$ symmetry[16] have been determined for all systems. Although data have been previously published on the SHG response of a number of side-chain polyphosphazene films,[10] the new compounds should allow for a much more stable response. Therefore, the thermal decay of the $\chi_{15}{}^{(2)}$ component of the second-order nonlinear susceptibility tensor for guest−host (**I**, **II**) and side-chain (**III**) systems has been investigated at various temperatures in the range room temperature (RT)−120 °C. The results will be discussed in light of current models that have been extensively applied to organic polymers.[14,17−23] The comparison between the three systems is expected to elucidate the role of the chemical and structural features of the chromophore−PPZ system on the SHG response and relaxation behavior. These features include chromophore size and its mode of incorporation to the polymer.

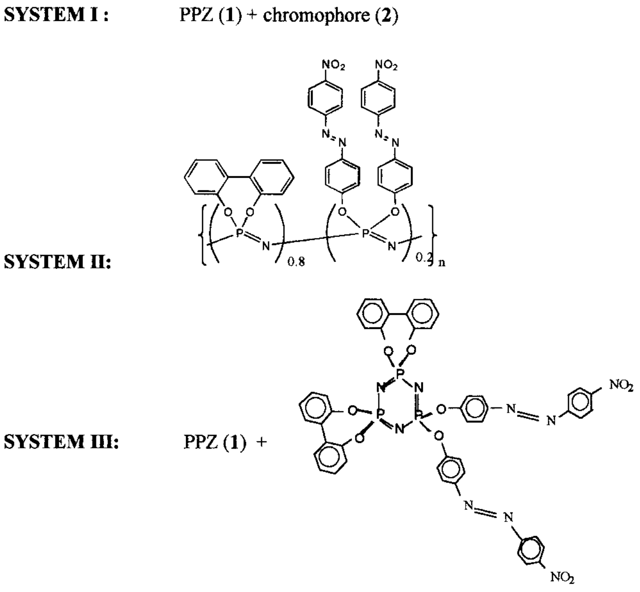


Figure 2. Chemical structures of systems **I**, **II,** and **III**.

2. Experimental Section

2.1. Films Preparation. The synthesis of PPZ polymers with a high glass-transition temperature (≥145 °C) has been previously reported.[12,13] Films of the three investigated systems incorporating the NLO chromophore have been, then, prepared by spin-coating a solution of the systems in chlorobenzene at

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Table 1. Components of the Second-Harmonic Susceptibility Tensor for Systems I, II, and III at a Poling Voltage (V_p) of 9 kV[a]

system	V_p (kV)	N (10^{20} cm^{-3})	$\chi^{(2)}_{15}$ (10^{-9} esu)	$\chi^{(2)}_{31}$ (10^{-9} esu)	$\chi^{(2)}_{33}$ (10^{-9} esu)	$\chi^{(2)}_{15}/N$ (au)
I	9	2.27	3.6 ± 0.4	4.1 ± 0.5	12.3 ± 1.4	1.59
II	7.2	21.2	1.2 ± 0.4	1.1 ± 0.3	3.6 ± 1.2	0.06
	9	21.2	5.0 ± 0.4			0.23
III	9	8.85	2.2 ± 0.3	2.3 ± 0.3	5.7 ± 0.8	0.2

[a] For system II the values for V_p= 7.2 kV are given for comparison. N stands for molecular concentration, and the last column gives the $\chi^{(2)}_{15}$ values normalized to equal concentration. (1 esu = 4.19×10^8 pm/V.)

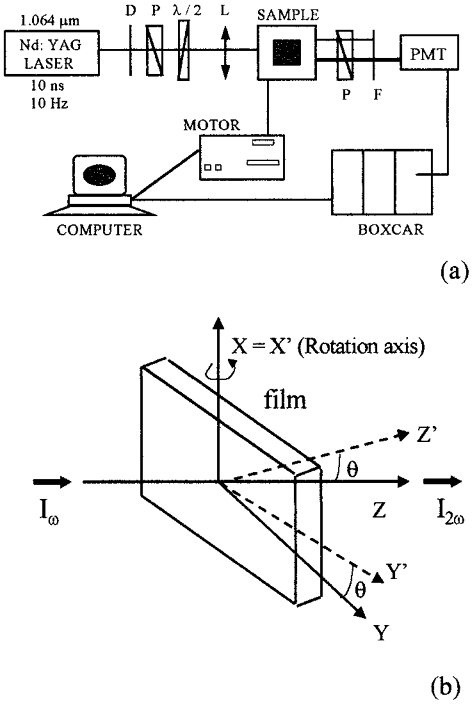

Figure 3. (a) Experimental setup and (b) film geometry.

weight concentrations of 6% on clean glass substrates. In the two guest–host systems the weight percentage of the guest to the host (polymer **1**) was 5% for system **I** and 30% for system **III**. These were the highest concentrations allowed by the guest (chromophore or cycle, respectively) solubility in the chlorobenzene solution. This solution was previously filtered to remove impurity particles, spun at 200–500 rpm, and finally baked at 90 °C for 5 h and subsequently kept at RT for 16 h. Spinning rates are much smaller than generally used, but they were found optimum for the preparation of our films. The baking and annealing processes were carried out in a vacuum to remove the solvent as completely as possible. The thicknesses obtained, measured with a profilometer, were in the range 0.5–2 μm. The NLO chromophore concentration for the three systems was also calculated by comparing their optical absorption spectra in spin-coated films with the one from the chromophore in a known concentration chloroform solution. The obtained values are given in Table 1.

2.2. Corona Poling. To induce molecular ordering in the spin-coated films, and so break their centrosymmetry, a corona poling technique was used.[14] A needle, at a static potential between 7000 and 9000 V, was positioned at ~1 cm above the grounded sample. The temperature during poling was ~140 °C, close to T_g in order to facilitate molecular orientation. The poling time was two and a half hours. Under these conditions a steady-state corresponding to thermodynamical equilibrium in the presence of the field appears to be achieved.

2.3. NLO Experimental Setup. The experimental setup and the film geometry are shown in Figure 3. The SHG intensity was detected as a function of the incidence angle of the laser beam, which is changed by rotating the sample with regard to an axis (X) in the film plane and perpendicular to the incident fundamental beam (Z). A Q-switched Nd^{3+}:ytrium–aluminum–garnet (YAG) laser, with a 10 ns pulse duration and a repetition rate of 10 Hz, operating at 1064 nm was used as fundamental light source.

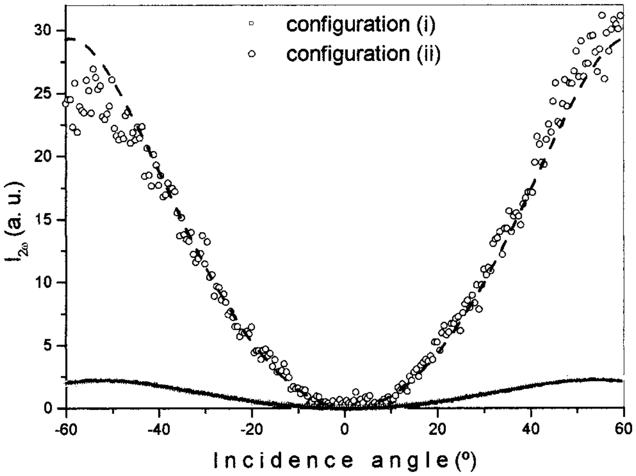

Figure 4. Maker fringes data for a film of compound **II** using configurations i and ii. The solid and dashed lines correspond to the best fittings to the theoretical expression (eq 2).

In front of the sample, a linear polarizer and a half-wave plate are used in order to obtain the three polarizations of the incident beam needed to determine the three independent components of the $\chi^{(2)}_{IL}$ tensor. Those polarizations are configuration i along the X axis, configuration ii along the Y axis, and configuration iii at 45° from either the X or Y axis. We also used a polarizer behind the sample to measure only one polarization component of the second-harmonic signal (see below). This signal is detected by a photomultiplier tube, averaged by a boxcar integrator, and stored in a computer. As an example, typical results for the SHG yield in configurations i and ii are shown in Figure 4.

Experiments with the same geometry, using an X-polarized incident beam and detecting also X-polarized second-harmonic signal were performed on an X-cut congruent LiNbO$_3$ plate to be used as a reference ($\chi^{(2)}_{33} = 1.96 \times 10^{-7}$ esu).

3. Physical and Optical Characterization

The molecular weight was 800 000 for the PPZ system incorporating the chromophore as a side chain (system **II**), whereas it was 500 000 for the undoped polymer (PPZ **1**) used as host (solvent) in systems **I** and **III**. These values were determined by gel permeation chromatography (GPC). The glass-transition temperatures measured by differential scanning calorimeter (DSC) were as follows: T_g = 144° C for guest–host system **I**, T_g = 145 °C for side-chain system **II**, and T_g = 139° C for guest–host system **III**. On the other hand, the glass-transition temperature for the undoped PPZ **1** was T_g = 156 °C. These results indicate that the solution of guest molecules into the polymer lowers the glass-transition temperature and makes it similar to that

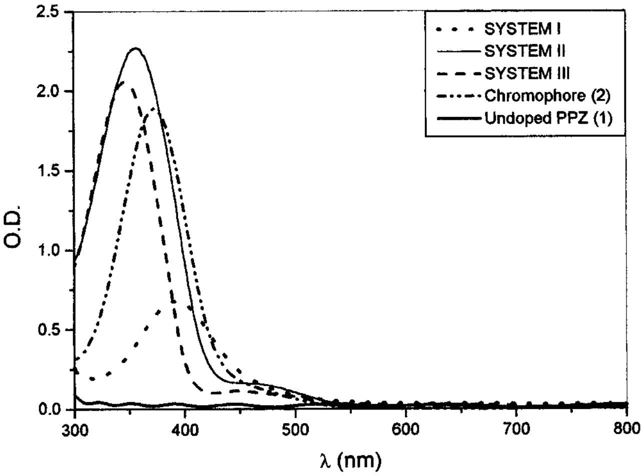

Figure 5. Optical absorption spectra for spin-coated films containing systems **I**, **II,** and **III**. The optical absorption spectra of undoped PPZ (**1**) and chromophore (**2**) in chloroform solution are also included for comparison.

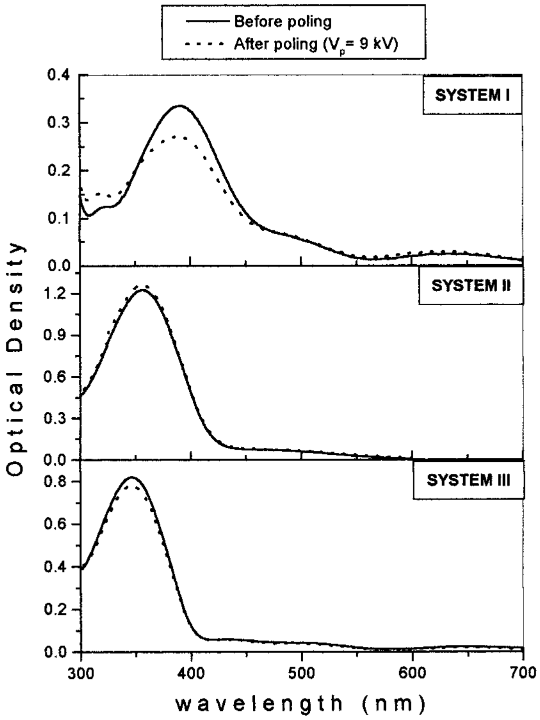

Figure 6. Effect of poling field (V_p = 9 kV) on the optical absorption spectra of systems **I**, **II,** and **III**.

corresponding to the side-chain polymer. No appreciable weight losses were detected by thermal gravimetric analysis (TGA) below T_g.

3.1. Optical Absorption Spectra. The optical absorption spectra for films of the three investigated systems are shown in Figure 5. The spectra for undoped PPZ (**1**) films and the chromophore (**2**) in chloroform solution are included for comparison. The main polymer has no appreciable absorption down to 300 nm. On the other hand, the films containing the chromophore have an intense band in the UV and a much weaker one in the blue region. However, the intense UV band in the films is considerably blue-shifted in comparison to that of the chromophore in chloroform solution, possibly in accordance with the polar character of this solvent. One also notes that system **I** presents a larger red-shift of the chromophore band in comparison to **II** and **III** polymers. The differences in peak wavelength among the three film systems should be related to the different structure and/or chemical link of the chromophore to the main PPZ chain. Anyhow, all systems still present a wide window in the visible and near-infrared ranges very useful for wave-mixing experiments.

The effect of poling on the film spectra is illustrated in Figure 6. This provides information on the molecular ordering achieved in the film. For the guest−host system I the height of the main absorption band considerably decreases with poling (near 25% for a poling field of 9 kV). This is the expected behavior when the dipole moment of the transition is parallel to the permanent ground-state dipole moment of the molecule. Under these conditions the chromophores orientate parallel to the poling field and so perpendicular to the film faces, therefore decreasing the absorption for the incident light. The relative change in absorption coefficient $\Delta\alpha/\alpha$ coincides with the order parameter $\phi = \langle P_2(\theta)\rangle$, P_2 being the second-order Legendre function and θ the angle between the molecular axis and the direction of the applied field. One can write[24,25]

$$\phi = \frac{\Delta\alpha}{\alpha} = \frac{3}{p}\coth(p) - \frac{3}{p^2} - 1 \qquad (1)$$

where $p = (\mu_0 \cdot E)/kT$, μ_0 being the molecular dipole moment (ground state) and E the magnitude of the applied field. Relative changes $\Delta\alpha/\alpha \sim 25\%$ are inferred from eq 1 and have been reported for molecules with dipole moments of ∼10 D in common poling fields of a few MV/cm[18,24,25] corresponding to $p \approx 2$. The situation is different for systems **II** and **III**. For the side-chain polymer **II** the absorption keeps essentially constant on poling or even experiences a small increase. For the guest−host system **III** a very small decrease is observed. The reason for this behavior is not clear although it may be related to the larger volume of the triphosphazene-chromophore group and to the higher rigidity of the side-chain group (see Discussion).

4. SHG Results

The $\chi^{(2)}_{\mathrm{IL}}$ values were determined from the analysis of the Maker fringes following the procedure given in previous references.[25,26] The formula giving the effective second-harmonic intensity as a function of the rotation angle θ can be expressed as[26]

$$I_{2\omega}(\theta) = \frac{64\pi^3\omega^2{\chi_{\mathrm{eff}}}^2{I_0}^2T}{{n_\omega}^2 n_{2\omega}c^3}\exp^{((-\alpha_{2w}L)/(2\cos\theta'))} \frac{\cosh\left(\frac{\alpha_{2\omega}L}{2\cos\theta'}\right) - \cos\left(\frac{\Delta kL}{\cos\theta'}\right)}{\left(\frac{{\alpha_{2\omega}}^2}{4} + \Delta k^2\right)} \qquad (2)$$

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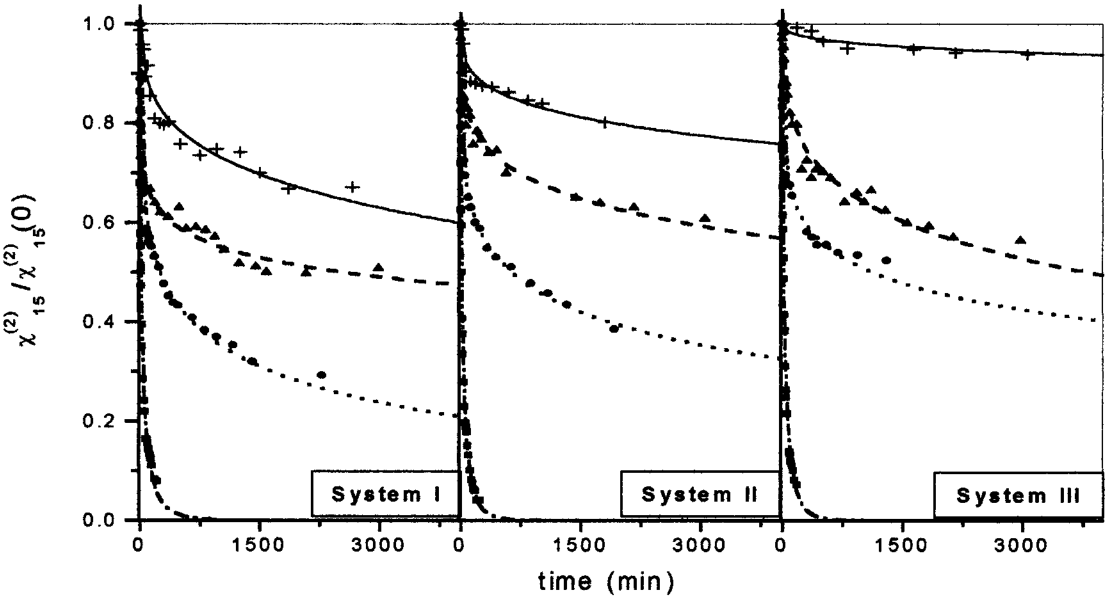

Figure 7. Relaxation behavior of $\chi^{(2)}_{15}$ normalized to the initial value for systems **I**–**III** at different temperatures: $T = 80$ °C (crosses), $T = 95$ °C (triangles), $T = 105$ °C (circles), $T = 120$ °C (squares). The lines stand for the best fittings to the KWW law. In the time scale used no appreciable relaxation is observed at RT for any of the systems.

I_0 being the incident fundamental intensity, L the film thickness, and T an overall transmission factor accounting for both fundamental and harmonic reflections at the various boundaries. θ' is the rotation angle inside the film ($\sin\theta' = 1/(n_\omega)\sin\theta$), and $\Delta k = k_{2\omega} - 2k_\omega = \{(2\omega)/c\}\Delta n$ is proportional to the index mismatch between the fundamental and harmonic frequencies. The absorption coefficient $\alpha_{2\omega}$ of the film at the harmonic frequency has been included in the analysis. Finally, $\chi^{(2)}_{\rm eff}$ is the effective SHG susceptibility corresponding to the polarization configuration used in the experiment, and it is expressed as[25]

configuration i [fundamental, X-polarized; second-harmonic, Y-polarized]:

$$\chi^{(2)}_{\rm eff} = -\chi^{(2)}_{31}\sin\theta' = -\chi^{(2)}_{31}\frac{\sin\theta}{n_\omega} \tag{3a}$$

configuration ii [fundamental, Y-polarized; second-harmonic, Y-polarized]:

$$\chi^{(2)}_{\rm eff} = -[(2\chi^{(2)}_{15} + \chi^{(2)}_{31})\cos^2\theta' + \chi^{(2)}_{33}\sin^2\theta']\sin\theta' \tag{3b}$$

configuration iii [fundamental, 45°-polarized; second-harmonic, X-polarized]:

$$\chi^{(2)}_{\rm eff} = -\chi^{(2)}_{15}\sin\theta' = -\chi^{(2)}_{15}\frac{\sin\theta}{n_\omega} \tag{3c}$$

By fitting expressions 2 and 3 to the experimental data, the values for the three nonzero components of the $\chi^{(2)}_{\rm IL}$ tensor have been independently determined. Results are listed in Table 1. The data obey the Kleinman rule as expected from the essentially off-resonant character of the excitation. Moreover, the relationship $\chi^{(2)}_{33} = 3\chi^{(2)}_{15}$, characteristic of linear (or Kleinman symmetry at molecular level) molecules in thermal equilibrium at low poling fields, is also approximately obeyed most clearly for the guest–host system **I**. When $\chi^{(2)}_{15}$ values are normalized to equal chromophore concentration, systems **II** and **III** present essentially the same response whereas system **I** shows a substantially larger second-order NLO susceptibility. This normalization does not have a physical meaning, and it is exclusively used as a practical way to compare the relative SHG susceptibilities of the three systems. This enhancement cannot be attributed to the red-shift of the absorption band in comparison to the other systems (see Figure 5), but it should be related to the higher degree of ordering achieved for system **I** during poling (see Discussion).

5. Thermal Relaxation of the SHG Response

The key feature of our PPZ systems is their high glass-transition temperature T_g in comparison to previously investigated polyphosphazenes.[8] In fact, the glass-transition temperature ranks in the high region of the scale of the reported transition temperatures.[16] The relaxation behavior of $\chi^{(2)}_{15}$ was monitored at various temperatures after poling. This component was selected because it is the easiest to be measured in relation to our reference measurement configuration. The comparative data for the three systems are shown in Figure 7a–c. All of our data points were taken after a few minutes from the end of the poling. Therefore, the anomalous initial contribution to the decay kinetics reported by several authors[20,21] is not present in our experiments. Before embarking ourselves in a more detailed discussion of the data, the simple inspection of the figure shows that for temperatures ≤105 °C system **I** relaxes faster than systems **II** and **III**. Curiously, guest–host system **III** shows a lower relaxation rate than side-chain system **II**. However, the differences in relaxation times are relatively modest and decrease with increasing temperature. At 120 °C all systems essentially present the same relaxation behavior. The decay curves can be reasonably well fitted to a biexpo-

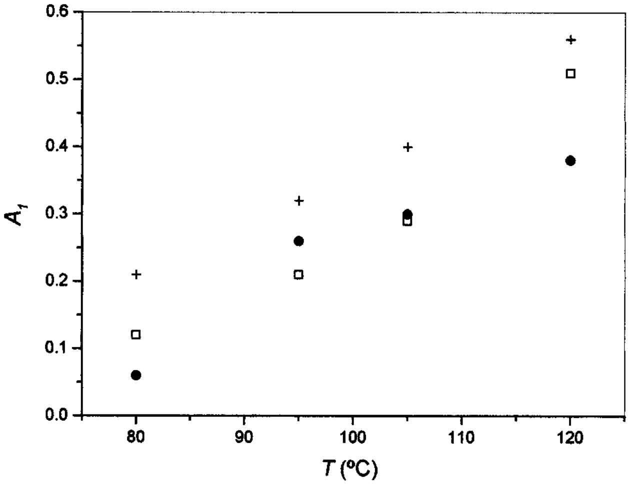

Figure 8. - Dependence of the fast biexponential amplitude, A_1, on temperature for systems **I** (crosses), **II** (squares), and **III** (circles).

nential kinetics[19,27,28]

$$\chi_{15}^{(2)}(T) = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2} \tag{4}$$

where τ_1, A_1 and τ_2, A_2, respectively correspond to the rates and amplitudes of the fast and slow components of the decay. Values for both fast τ_1 and slow τ_2 relaxation times are not much different for the three compounds, and differences are not systematic. The ratios τ_2/τ_1 are typically around 100 (except for 120 °C where it amounts to ~10). However, the amplitude A_1 of the fast component is clearly higher for the guest–host system I than that for the other polymers, as illustrated in Figure 8. This suggests that the guest–host system I presents an enhanced fast initial relaxation (see Discussion).

The relaxation data can also be fitted to a stretched exponential or Kohlrausch–Williams–Watts (KWW) law[29,30]

$$\chi_{15}^{(2)}(T) = A e^{-(t/\tau)^{b}} \tag{5}$$

where τ is the characteristic relaxation time and β is a stretching parameter that varies between 0 and 1. The fitting is illustrated in Figure 7. The relaxation times τ are comparable to the slow time constant τ_2 in the biexponential decomposition (eq 4). On the other hand, the β values obtained from the fitting increase with temperature and range from 0.30 for 80 °C to 0.55 for 120 °C. This increase has been also found in previous experimental work.[20,31,32]

The accordance of our data with both kinetics laws, biexponential or stretched exponential, are reasonably good although in a few cases somewhat better fittings have been obtained after adding a constant term to the right-hand side of eqs 4 and 5. Since the KWW kinetics is most often used to discuss the relaxation data, we will focus our Discussion section on this relaxational model.

6. Discussion

From the last column of Table 1 one observes that after normalization of the $\chi_{15}^{(2)}$ values to equal chromophore concentration the guest–host system I yields the highest values. As commented in section 4, this enhancement cannot be attributed to the longer wavelength of the absorption peak in comparison to the other systems. In fact, the effect may be related to the large reduction measured in the absorption coefficient under poling, suggesting a strong alignment parallel to the field. For systems **II** and **III** this efficient alignment is not achieved, accounting for the lower values of the measured susceptibilities. The higher SHG efficiency of guest–host in comparison to side-chain systems has been also observed in experiments comparing the 4-(dicyanovynyl)-4′-(dialkylamino)azobencene (DCV) chromophore incorporated in PMMA.[33] This result was also attributed to a better ordering in the guest–host system in comparison to the side-chain one. Our data about the effect of poling on the absorption spectra clearly confirm that a more efficient poling for the guest–host system **I** is responsible for its superior SHG response. The lower second-order NLO susceptibilities achieved for polymers **II** and **III** can be correlated with correspondingly lower order parameters and could be attributed to the effect of enhanced electrostatic chromophore interactions at high doping levels.[34,35] However, other causes can also contribute, such as an enhanced rigidity of the side-chain group in system **II**. The difficulty to pole the side-chain polymers has been associated with the restricted rotational freedom of the side groups.[36] For our side-chain polymer (system **II**), this effect is further complicated by the paired structure of the side group (see Figure 2). Anyhow, the constancy or even small increase of the optical absorption with poling for the side-chain polymers may be understood as follows. The poling field applied at $T < T_g$ induces some partial alignment of segments of the main polymer chains along a direction parallel to the field and so perpendicular to the film faces. If the side groups were rigidly attached in a perpendicular direction to the main chain, they would become oriented parallel to the film faces and therefore would contribute to an enhanced absorption. This effect would compete with the decrease caused by the (partial) parallel orientation of the chromophores themselves, if they are assumed to possess a certain degree of flexibility. Possibly, the incorporation of a spacer group between the side chain and the main PPZ chain may help to enhance the flexibility of the side-chain group and facilitate their orientation parallel to the field.[36] Moreover, it may also contribute to decouple the electron-

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withdrawing characteristics of the PPZ backbone from those of the donor−acceptor substituted side chain[36] and increase the polar character of the group. This may also lead to higher values of the second-order NLO susceptibilities than those measured in this work.

On the other hand, the $\chi^{(2)}_{\mathrm{IL}}$ values obtained for the guest−host system **III** are also smaller than those measured for system **I** and similar to those for polymer **II**. This correlates with the lower degree of order induced in system **III** during poling similar to the side-chain system **II**. In this case, one can argue that the triphosphazene-chromophore group should have a much lower rotational mobility owing to the higher molecular volume as observed in other studies.[37]

Aside from the above considerations, the susceptibility values $\chi^{(2)}_{33}$ measured for our side-chain PPZ (∼6 pm/V) are similar to those reported by Allcock[9] for nitrostilbene-substituted PPZ although considerably lower than those for nitroazobenzene-substituted polyphosphazenes. However, one should note that for this chromophore the absorption maximum occurred at 490 nm and so the susceptibilities are strongly resonant at the harmonic frequency (532 nm) for fundamental excitation at 1064 nm. It should be also remarked that in previous work[10] only the $\chi^{(2)}_{33}$ coefficient was reported. It was inferred from the directly measured $\chi^{(2)}_{31}$ coefficient under the assumption of low poling fields and Kleinman symmetry condition ($\chi^{(2)}_{33} = 3\chi^{(2)}_{31}$). In our experiments the three components $\chi^{(2)}_{31}$, $\chi^{(2)}_{15}$, and $\chi^{(2)}_{33}$ are independently measured so that the validity of the Kleinman rule can be tested. In fact, it is reasonably well obeyed. It is also instructive to compare the values measured for our guest−host system with those reported for the organic polymer PMMA containing the DO3 chromophore at similar concentration.[38] Values in both cases are around 5 pm/V, showing equivalent performances of the inorganic (PPZ) and organic (PMMA) hosts.

Our $\chi^{(2)}_{\mathrm{IL}}$ values are in the same range as those previously obtained for PPZ doped with NLO chromophores, but they present a definite advantage owing to their higher T_g and superior thermal stability of the NLO response. At RT, our side-chain polymer **II** does not show an appreciable decay in about 3 months. One interesting feature of our work is the comparison of the relaxation of the guest−host and side-chain polymers containing the same chromophore. Very few works offer this comparison. The data on DCV in PMMA show a dramatic difference in the relaxation behavior[33] for the two kinds of polymers. The side-chain polymer is stable at RT over 1 month, whereas the guest−host decays to almost 30% of the initial value in 5 days. This marked difference is related to the strong decrease in the glass-transition temperature associated with the introduction of the guest molecules that lead to plasticization of PMMA.[39] In our experiments the differences found in the relaxation behavior between guest−host (system **I**) and side-chain (system **II**) polymers are much less relevant than for the PMMA/DCV system[33] in accordance with the very small reduction in T_g caused by the guest compound.

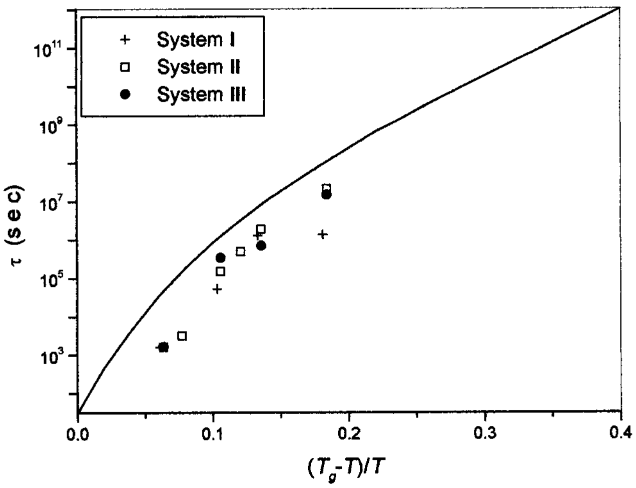

Figure 9. Plot showing the dependence of the relaxation time on $(T_g - T)/T$ to test the Addam−Gibbs behavior. The solid line stands for the curve obtained in ref 20 for a number of organic polymers.

From the fitting of our decay curves to the KWW law, the relaxation time τ and the stretching exponent β have been determined as a function of temperature. As previously found,[20] this latter parameter decreases with increasing temperature ($\beta \approx 0.55$ for 120 °C and $\beta \approx 0.3$ for 80 °C for all systems). As for the dependence of τ on temperature, a variety of functional decay forms have been proposed and used in the previous literature. Some recent analyses[20,21,23] use a model based in the Adams−Gibbs formulation for the configurational entropy of the relaxing polymer segments. This leads to the following expression for the structural relaxation time[40]

$$\tau = \tau_0 \exp\{B/T(1 - T_2/T_f)\} \qquad (6)$$

where B represents an activation energy divided by the gas constant R and T_2 is the temperature where the configurational entropy of the polymer vanishes. T_f stands for a fictive temperature that measures the degree of deviation from thermal equilibrium. In fact, a number of different side-chain, main-chain, and guest−host polymers have been shown to fit a remarkable scaling curve when the relaxation time is plotted as a function of $(T_g - T)/T$ or T_g/T.[14,20,21,23] Therefore, the relaxation times (τ) for our three systems **I**, **II**, and **III** have been plotted in Figure 9 as a function of $(T_g - T)/T$. Unfortunately, we cannot make a quantitative thermodynamical analysis of those data since we lack information on the parameters T_2 and T_f appearing in eq 6. However, in order to see whether the data points for our PPZ polymers obey this scaling behavior, the Adams−Gibbs curve obtained in a detailed previous work[20,21] has been included for comparison in Figure 9. Our points follow the same trend although relaxation times are about 1 order of magnitude shorter than those measured for a number of organic polymers.

One should note in accordance with other authors that guest−host systems show a lower τ than side-chain polymers for $T \ll T_g$. This faster relaxation of the guest−

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host polymers is more clearly appreciated when using a biexponential analysis. Here, a significant initial rapid decay appears that is not (or less) observed in side-chain polymers. This behavior may be related to a contributing β relaxation associated with chromophore reorientation occurring at low temperature.

7. Summary and Conclusions

The potential for SHG applications of spin-coated films of novel polyphosphazenes with high glass-transition temperatures has been evaluated. The measured susceptibilities $\chi_{31}^{(2)}$, $\chi_{15}^{(2)}$, and $\chi_{33}^{(2)}$ are comparable to those previously obtained with other PPZ having a lower T_g. For a competitive performance in practical devices, those values should be substantially increased. The approximate validity of the Kleinman conjecture ($\chi_{31}^{(2)} \approx \chi_{15}^{(2)}$) has been directly ascertained. The guest–host system I containing the free chromophore in solution yields the highest second-order NLO susceptibilities for equal concentration in comparison to the other systems. This is in accordance with a higher degree of molecular ordering achieved during poling as confirmed by measuring the effect of poling on the absorption spectra. The susceptibility values are comparable with those previously obtained on PPZ with much lower glass-transition temperatures and so less stability. Detailed data on the relaxation behavior have been obtained for temperatures in the range RT–120 °C. Decay curves can be well fitted to either a biexponential or a stretched exponential (KWW) law. Using this latter model the data for the lifetime τ roughly fit (except for a reduction factor) the scaling behavior observed in previous work. Also the stretching exponent β follows the reported trend with temperature. At low enough temperatures $T \ll T_g$, the guest–host polymer **I** presents an important rapid initial decay that is much less significant in the side-chain system **II** and the guest–host system **III**. In conclusion, poled films of novel high-T_g polyphosphazenes constitute useful optical materials with a wide transparency window and a high thermal stability after poling, although their SHG capabilities should be improved for devices applications.

Acknowledgment. Financial support from CYCIT (Project TIC-96-0668), DGICYT (Project PB97-1276), and FICYT (Project PBMAT98-02) is gratefully acknowledged.

CM001038D