

Poly(vinylpyridine) and Related Polymers as Guests for Organotransition-Metal-Based NLO Chromophores

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We have investigated a set of three polymers functionalized by tungsten pentacarbonyl as a chromophore for second harmonic generation (SHG). Films were poled by the Corona poling method, and their second-order nonlinear responses were measured via in situ SHG while poling. It is found that poly(vinylpyridine) can be used as a probe to obtain the sign of the hyperpolarizability coefficient of the chromophores (β). These polymers all exhibit modest SHG properties. This raises several interesting theoretical and practical questions which are discussed: thermal stability, effect of a negative sign of β , importance of the chromophore dipole moment, and poling efficiency of chromophores based on tungsten pentacarbonyl. Relaxation mechanisms are also discussed in relation to the structure of the polymers backbone.

Introduction

The study of polymers involving constituent nonlinear optical (NLO) chromophores aligned with an electric field has been the subject of intense interest in the search toward new materials for second harmonic generation (SHG).^{1–4} It is now well established that the chromophores must be bonded to the polymer framework or placed in a high- T_g polymer if the material is to exhibit a SHG stability over time.^{5,6} Soft Lewis base polymers offer many possibilities of forming linkages between polymeric and potential organometallic chromophores. On the other hand, only a few organometallics have been studied for their nonlinear properties.^{7–13} Compared to the more common organic molecular chromophores, they generally exhibit modest molecular nonlinearities (β_{ijk}) for reasons that are becoming increasingly clear.¹⁴ Nevertheless, organometallic chromophores offer a number of unusual properties which might bring about NLO materials with

unique characteristics,¹⁵ unusual magnetic and electrochemical properties, the possibility of cross-linking methods within polymer hosts, a novel way of incorporating chromophores in polymer hosts, and also a sensitivity to various reagents that could result in selective NLO waveguide detectors. Ferrocene-based polymers have been recently prepared, and their NLO properties investigated.¹⁶

The goal of the present contribution is to investigate the properties of a set of novel polymers in which organometallic units are chemically bounded and ori-

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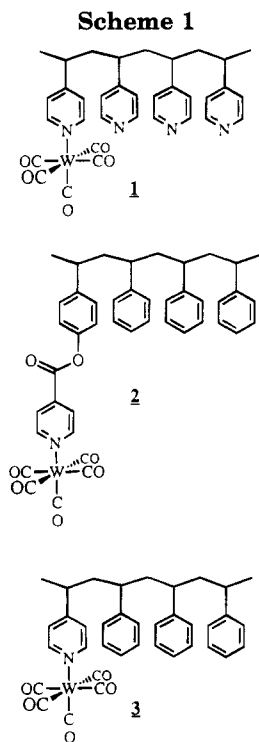
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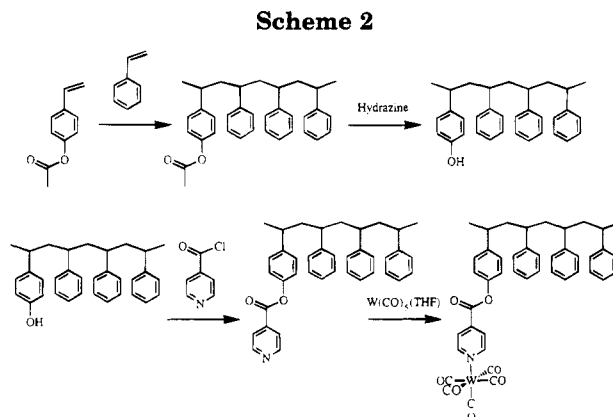


ented by electric field poling. We focus on several interesting aspects of this problem: the design of materials with SHG properties involving the polymer framework itself, the response of such chromophores in an electric field, and the role of the polymer backbone in the relaxation process. We selected $(\text{CO})_5\text{W}(\text{pyridine})$ as a model organometallic chromophore structure. It is easily incorporated into soft Lewis base polymers such as poly(vinylpyridine),¹⁷ and the air stability as well as the glass transition temperatures of the resulting polymers render them suitable candidates for further physical studies including the behavior at high temperature in the presence of a strong electric field. This may be a potential limitation for the use of organometallic chromophores in poled polymers. Following the first results, several improvements in the properties of our system were achieved and eventually a set of three polymers has been investigated. Their structures are shown in Scheme 1.

Experimental Section

Starting Materials and Equipment. $\text{W}(\text{CO})_6$ was purchased from Aldrich as were styrene, 4-vinylpyridine, *p*-acetoxystyrene, and isonicotinoyl chloride. Poly(4-vinylpyridine) ($M_w = 120\,000$) was purchased from Polysciences Inc. Every starting material was used as received except 4-vinylpyridine, which was distilled under reduced pressure and stored under argon at $-30\text{ }^\circ\text{C}$ to avoid spontaneous polymerization. Photolysis and synthesis involving the $\text{W}(\text{CO})_5$ fragment were carried out under nitrogen, but the purifications by repeated precipitations were made in air.

IR spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Glass transition temperature measurements were performed under nitrogen by differential scanning calorimetry on a Perkin-Elmer DSC-2 calorimeter using about 10 mg of sample. The scan rate was $5^\circ/\text{min}$. ^1H NMR spectra were recorded on a Varian XL 400 spectrometer, but the very



broad lines of the functionalized polymers made quantitative determinations of functionalization levels inaccurate.

Polymer Synthesis. Poly(4-vinylpyridine- $\text{W}(\text{CO})_5$) (**1**). The synthesis was achieved following a literature procedure.¹⁷ $\text{W}(\text{CO})_6$ was first photolyzed in absolute EtOH using a high-pressure mercury lamp and a Pyrex glass reactor. This solution was then added under nitrogen to an ethanolic solution of poly(4-vinylpyridine). Different molar ratios (tungsten/pyridine) were selected: 1/20, 1/15, 1/10, and 1/5. After stirring overnight under nitrogen, the solvent was removed under vacuum at $30\text{ }^\circ\text{C}$, and the crude yellow polymers were purified by three precipitations from CH_2Cl_2 (in which unbound W monomers are soluble) with hexane, following by vacuum drying. Spectroscopic methods (IR, UV) verified that the $\text{W}(\text{CO})_5$ chromophore moieties are bonded to the polymers.¹⁵

ratio W/py	calc.				found			
	C	H	N	W	C	H	N	W
1/20	71.76	5.82	11.55	7.58	72.15	6.31	11.52	7.40
1/15	69.50	5.57	11.05	9.67	69.82	6.12	10.89	9.27
1/10	65.49	5.13	10.19	13.37	65.90	5.68	10.28	13.12
1/5	51.46	3.75	7.50	21.64	50.62	4.16	7.63	20.37

Poly $\text{W}(\text{CO})_5$ -(4-Vinylphenyl isonicotinoate) Copolymer with Styrene (2) (Scheme 2). Four functionalization levels (pyridine/styrene) were selected: 1/20, 1/15, 1/10, and 1/5. The copolymer styrene-hydroxystyrene was synthesized in two steps using a slight modification of the procedure described in the literature:¹⁵ 10 g of the appropriate mixture of styrene and *p*-acetoxystyrene were copolymerized under argon at $80\text{ }^\circ\text{C}$ with 100 mg of AIBN as a radical initiator. The crude polymers were purified by two successive dissolutions in 75 mL of toluene followed by precipitation with a 10-fold excess of methanol. After filtration, the polymers were dried under vacuum ($p < 10^{-3}$ Torr) at $60\text{ }^\circ\text{C}$ overnight. The yield of the polymerization was found to be 50–60% for all the reaction mixtures. According to the reactivity ratios r_1 (*p*-acetoxystyrene) = 1.18 and r_2 (styrene) = 0.88,¹⁹ we assume that the composition of the polymers are close to what they are in the molecular mixture.

ratio acetoxy/hydroxy	calcd		found	
	C	H	C	H
1/20	90.93	7.58	90.83	7.58
1/15	90.48	7.54	90.28	7.61
1/10	89.62	7.47	89.61	7.59
1/5	87.20	7.27	86.83	7.34

The four copolymers were converted to the corresponding poly(hydroxystyrene) copolymers with hydrazine hydrate as described previously.¹⁹ Four samples of 4-vinylphenyl isonicotinoate-styrene copolymers were eventually obtained by esterification of the copolymers using isonicotinoyl chloride in

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pyridine. For 1 g of each styrene-hydroxystyrene copolymer dissolved in 40 mL of dry pyridine, an equimolar amount of triethylamine (per hydroxy group) was added, as was a 50% excess of isonicotinoyl chloride in 25 mL of dry pyridine. The solutions were refluxed for 24 h and, after cooling, a stoichiometric amount of Et_3NHCl was filtered off. The polymers were then precipitated into 1.5 L of water, filtered, and washed with water. Purifications were achieved by repeated precipitations with water from THF solution. The samples were dried under vacuum at 100 °C for 24 h.

ratio pyridine/styrene	calcd		found	
	C	H	C	H
1/20	90.46	7.45	90.92	7.92
1/15	89.92	7.37	89.94	7.84
1/10	88.85	7.20	88.95	7.89
1/5	86.06	6.75	86.43	7.63

The metal carbonyl fragment was introduced using the general procedure described for **1**. A 33% excess of $\text{W}(\text{CO})_5$ (THF) in THF was stirred overnight in the dark with the appropriate copolymer under argon. The polymer was then precipitated into deoxygenated hexane which is a solvent for $\text{W}(\text{CO})_5(\text{THF})$ but not for the functionalized polymers. Purification was achieved by repeated precipitations with hexane from THF solutions. Incorporation of the $\text{W}(\text{CO})_5$ fragment was verified by IR spectroscopy, by the easily identifiable CO band at 1930 cm^{-1} , which is consistent versus that expected for most $\text{W}(\text{CO})_5$ fragments bound to the nitrogen atom of a substituted pyridine.²⁰ Elemental analysis indicates in any case a functionalization level of ~33% of the available ligand units, giving a final ratio of tungsten per styrene unit of approximately 1/60, 1/45, 1/30, and 1/15.

ratio W/styrene	calcd			found		
	C	H	W	C	H	W
1/60	87.10	7.11	2.65	87.47	7.30	2.50
1/45	85.60	6.92	3.42	86.14	7.14	3.07
1/30	82.87	6.59	4.82	83.53	6.76	4.11
1/15	76.36	5.78	8.18	77.21	6.11	7.58

Vinylpyridine- $\text{W}(\text{CO})_5$ Copolymer with Styrene (3). Following the same method as describe above, (4-vinylpyridine)- $\text{W}(\text{CO})_5$ was first isolated and recrystallized from methanol as described in the literature.^{17b} Then, it was bulk copolymerized with styrene using AIBN as a radical initiator at 75 °C for 75 min. Composition of the monomer mixture: 2 g of styrene, 137 mg of (4-vinylpyridine)- $\text{W}(\text{CO})_5$, 50 mg of AIBN. This composition assumes a ratio of 1 tungsten/60 styrenes (however it was found that the coordination of the vinylpyridine significantly increases the speed of polymerization). This modification is consistent with previously reported observations.²¹ The crude polymer was purified as was **1** (vide supra). IR and UV spectra were used to check that the $(\text{CO})_5\text{W}$ fragment was incorporated into the resulting polymer and were consistent with the reported data.¹⁷ The ratio W/styrene in the polymer was found to be close to 1/18. Anal. Calcd: C, 81.05; H, 6.55; N, 0.64. Found: C, 82.40; H, 6.75; N, 0.63.

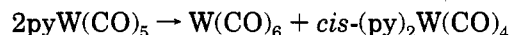
SHG Measurements. Casting of films for optical studies was achieved by the following procedure: Two drops of a concentrated solution of the subject polymer in ethanol or THF were applied to an indium tin oxide (ITO) coated glass slide to give a transparent film after slow evaporation (thickness ~1 μm). The samples were dried under vacuum (10^{-2} Torr) for 2 days at room temperature and then for 3 days at 60 °C. The film thickness was measured with a Tencore Alpha-Step 200 surface profiler. The in situ SHG/poling procedure used for this study has been described previously.²² The details of the procedure were the following: In the presence of a + 4.0

kV potential, the samples were heated at 70 °C for 30 min. This short time was enough to reach an apparent maximum value of the SHG intensity and prevented slow decomposition which was observed to occur for several samples poled at temperatures above 100 °C. No apparent damage to the films was observed during the poling process. A decrease of the signal amplitude was invariably observed while still under the field as the temperature was lowered, so the efficiencies are reported as calculated d_{33} values recorded in situ at 70 °C. The decay of the SHG signal was studied as a function of the time at room temperature after an initial 15 min after poling field turned off.

Results and Discussion

Thermal Stability of the $\text{W}(\text{CO})_5\text{L}$ Chromophores.

An important question related to the use of organometallic chromophores in poled glassy polymers is their stability upon heating at a relatively high temperature under a strong corona electric field. Some group 6 metal carbonyl compounds are stable at rather high temperatures (for example, (benzene) $\text{Cr}(\text{CO})_2\text{P}(n\text{-Bu})_3$ incorporated into a polymer was reported to be stable up to 250 °C).²³ On the other hand, NLO properties were never observed for such a system and chromophores based on (benzene) $\text{Cr}(\text{CO})_3$ have been observed to have only modest β values.^{10c,24} Therefore we selected py- $\text{W}(\text{CO})_5$ as the chromophoric substituent of our polymers because derivatives of this molecule were already known to have more substantial β values based on a $d-\pi^*$ charge transfer from the metal to the pyridine ring.¹⁰ Tungsten was chosen instead of chromium or molybdenum because of the generally greater air stability of its complexes. At room temperature $\text{W}(\text{CO})_5$ derivatives have been found to exhibit considerable air stability even in solution. In regard to thermal stability, the literature^{17a} reports a thermolysis of **1** according to anticipated equation:



To investigate the magnitude of this effect, experiments can be conducted in which the polymer is heated at different temperatures under vacuum, and the infrared spectrum periodically examined. Upon heating above 140 °C, the ν_{CO} transition (1930 cm^{-1}) of the py- $\text{W}(\text{CO})_5$ species²⁰ is reported to decrease greatly while two new bands appear at 1810 and 1855 cm^{-1} , consistent with the formation of a $\text{py}_2\text{-W}(\text{CO})_4$.^{17a,25} Although this process in principle offers a potentially useful cross-linking mechanism that might enhance the temporal stability of d_{33} , it also decreases the chromophore number density. Furthermore, although (1,10-phenanthroline) $\text{W}(\text{CO})_4$ has a significant β value, that of $\text{cis-py}_2\text{-W}(\text{CO})_4$ is considerably less efficient than that of py- $\text{W}(\text{CO})_5$.²⁶ Therefore, thermal redistribution must be avoided.

We carefully checked by infrared spectroscopy that the poling procedures did not result in any decomposition of the chromophores even when irradiated by the laser beam at 80 °C for 1 h. A sample kept at 80 °C for

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1 day without the laser beam did not undergo any decomposition, but we noticed that the thermal redistribution was important at 120 °C after a few hours even without the laser.

Origin of the NLO Signal in Poled Polymers.

Before proceeding to describe our results, it is useful to describe briefly some of the fundamental principles of SHG in poled polymers. Nonlinear polarization can be induced by the strong electric field of laser beams as²⁷

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots$$

The macroscopic second order susceptibility is related to molecular hyperpolarizability β by

$$\chi^{(2)} = N\beta f(\omega) f(\omega) f(2\omega) O(\theta)$$

where N is the concentration of chromophores, $f(\omega)$ are local field factors at frequency ω , and $O(\theta)$ is an orientation factor taking into account the position of the chromophore (θ is the angle between the dipole moment of the chromophore (μ) and the poling field (E)).²⁸ In poled polymers,^{29–31} most of the $\chi^{(2)}$ components vanish, and SHG measurements are usually expressed by the second harmonic coefficient d_{33} ($=1/2\chi$) through

$$d_{33} = 1/2(N\beta F \langle \cos^3 \theta \rangle)$$

F is the product of all local field factors, $\langle \cos^3 \theta \rangle = \mu E / 5kT$. It has to be emphasized that although β is the origin of the NLO properties at the molecular level, it is not the only parameter to take into account in the poled polymer response, which is proportional to the $N\mu\beta$ factor.

SHG Efficiencies of the Polymers. (i) *SHG Efficiency of Poly(4-vinylpyridine).* PVP free of chromophore was found to exhibit a surprisingly large efficiency ($d_{33} \sim 1.5 \times 10^{-9}$ esu) after being poled above its glass transition temperature (>100 °C) for 1 h. Pyridine itself is a very modest chromophore ($\beta = +0.3 \times 10^{-30}$ esu).^{10c} However, it is highly concentrated in the bulk material, which can explain this value. Therefore, the side groups of the polymers are not innocent in NLO measurements, and the pyridine moieties must be taken into account if organometallic chromophores are bounded to the polymer.

(ii) *SHG Properties of 1.* The behavior of this composite polymer is a contribution of two components $d_{33} = d_{33}(\text{poly(vinylpyridine)}) + d_{33}(\text{(CO)}_5\text{W-py})$. On the basis of the molecular data (β recorded by EFISH and μ) reported in Table 1, the expected d_{33} values can be calculated at any functionalization level as $d_{33} \propto N_1\mu_1\beta_1 + N_2\mu_2\beta_2$, where 1 and 2 stand for the pyridine and

Table 1. Molecular Hyperpolarizabilities (β_{vec}) and Dipole Moments (μ) According to Ref 10c^a

	β (in 10^{-30} esu)	μ (in 10^{-18} esu)
pyridine	+0.3	2.3
acetylpyridine	<0.2	2.7
(CO) ₅ W(butylpyridine)	-3.4	7.3
(CO) ₅ W(acetylpyridine)	-9.3	4.5

^a The sign of β arrives from $\Delta\mu (= \mu_e - \mu_g)$, difference in the dipole moments between the excited state and the ground state in the electronic transition.

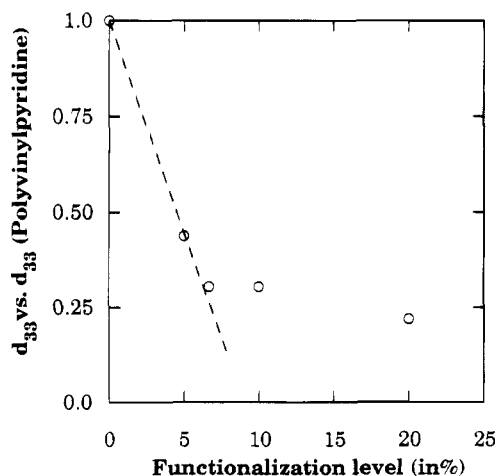


Figure 1. Plot of polymer 1 d_{33} values at different functionalization levels. The reference is poly(vinylpyridine) free of tungsten, poled for 30 min at 70 °C ($d_{33} = 8.2 \cdot 10^{-10}$ esu). The dotted line gives the expected d_{33} values as $d_{33} \propto N_1\mu_1\beta_1 + 0.28(N_2\mu_2\beta_2)$, which assumes a NLO response proportional to the chromophore concentration (see text for explanation).

(CO)₅W-py moieties, respectively. It must be pointed out that the use of poly(4-vinylpyridine) allows the determination of the sign of β of the chromophore, which is not usually accessible in poled polymers but which is known to be negative from EFISH experiments recorded for the substituted (CO)₅W-(pyridine) units. When this sign is opposite to that of the polymer, the SHG signal decreases when the concentration of the chromophore is increased. However, at higher concentrations, the SHG intensity should increase again, for it is dominated by the contribution of the chromophore. The d_{33} values recorded for polymer 1 at different functionalization levels are shown in Figure 1. The agreement between calculation and experiment is far from being excellent. However, the calculated d_{33} values assume that the poling of the large inorganic (CO)₅W fragments is as efficient as that of the small pyridine units. On the other hand, the size of pyridine is so small versus that of py-W(CO)₅ that the higher dipole moment of py-W(CO)₅ might be irrelevant when comparing the poling efficiency. A better agreement is obtained using $d_{33} \propto N_1\mu_1\beta_1 + 0.28(N_2\mu_2\beta_2)$, assuming the poling of the organometallics units being roughly 3 times less efficient than that of the pyridine units. The measurements of the glass transition temperatures (T_g) may support this observation. T_g values usually decrease as the length of the side group increases. This is a well-established trend for many polymer systems with non-polar side groups such as methacrylate ester, attributed to the generation of additional free volume by pushing the polymer main chains further apart from one another.³² However, with polar side groups such as most second order NLO chromophores, this statement is not

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Table 2. Glass Transition Temperatures (T_g) for Polymers 1 and 2 Measured by Differential Scanning Calorimetry (DSC)^a

1	T_g (°C)	2	T_g (°C)
ratio W/pyridine		ratio W/styrene	
0	107	0	109
1/20	117	1/60	112
1/15	124	1/45	115
1/10	no T_g observed	1/30	119
1/5	no T_g observed	1/15	no T_g observed

^a No transition was observed for polymer 3.

valid. In the case of the present polymers, the side chain forces of the inorganic fragments may dominate the backbone forces. The glass transition temperatures of polymer 1 are reported in Table 2. The unusual increase of T_g associated with a broadening DSC signal at higher functionalization level may have several origins (i.e., size of the side groups, crowding, etc.). It should also suggest that the chromophores may prefer to aggregate in areas rich in tungsten, where the poling process is less efficient.

(iii) *SHG Properties of 2.* The enhancement of the molecular hyperpolarizability (β) strongly depends on chemical modifications.³³ Versus 1, two modifications are achieved in the polymer structure, which are expected to enhance the NLO response. Most of the unbonded pyridine is removed; therefore, the deleterious competition of the polymer backbone is avoided. In addition, the increasing trend of β (magnitude) with the increasing withdrawing effect of ring substituents has been observed in the tungsten pentacarbonyl pyridine series. On the other hand, it has been emphasized above that β is not the only parameter to take into account in the polymer response, which is proportional to $\mu\beta$. It can be seen from Table 1 that an increase of the absolute β value (from 3.4 to 9.3×10^{-30} esu) results in a decrease of the dipole moment (from 7.3 to 4.5×10^{-18} esu). This behavior is unusual for organic chromophores exhibiting large β values, which are usually associated with large dipole moments, but takes place here where the NLO properties are based on a d- π back-coordination. It clearly appears that these two effects are working against one another, the value of the $\mu\beta$ product remains low, and so does the poling efficiency. This aspect offers an interesting opportunity to point out that in the search for new materials exhibiting second-order nonlinearity two levels of optimization must be considered. The molecular level (β) and a macroscopic level where the efficiencies in a poling process are directly proportional to the dipole moment. In this respect, (CO)₅W(substituted pyridine) chromophores seem not to be suitable candidates even if they may be associated with quite large β values in some cases.

The recorded data are shown in Figure 2. The shape of the graph is typical of that of a guest/host system. Using the data recorded on polymers 1 as references and assuming the same relation between d_{33} , μ , and β at low functionalization level, an agreement could be found assuming $d_{33} \propto N_1\mu_1\beta_1 + 0.2(N_2\mu_2\beta_2)$. It must be

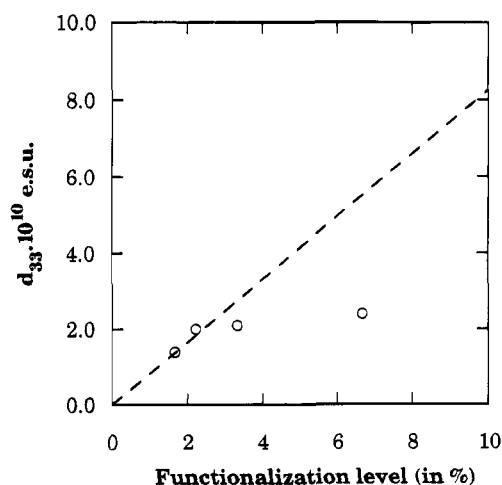


Figure 2. Plot of polymer 2 d_{33} values at different functionalization levels. The dotted line gives the expected d_{33} values as $N_1\mu_1\beta_1 + 0.2(N_2\mu_2\beta_2)$ which assumes a NLO response proportional to the concentration of the chromophore (see text for explanation). μ and β are reported in Table 1. The very poor agreement between dotted line and experimental data proves the inefficiency of the poling process at higher loading level.

pointed out that the poling efficiency of the organometallic moieties is lower in 2 than in 1. For a polymer more than 2% functionalized, the graph shows that the SHG efficiencies are almost independent on the loading level. It might be argued that poling could become inefficient due to increasing conductivity of the materials. We carefully checked that the conductance of the films at 70 °C was always lower than $10^{-7} \Omega^{-1}$ at any loading level.

Decay Rate of the NLO Signal. The most surprising property of 1 is the extremely rapid rate of decay of the SHG signal exhibited at all functionalization levels. When the poling field is turned off, all nonlinearity is lost in less than 1 min. This behavior, which is also observed in poly(vinylpyridine) free of tungsten but not in 2, seems to be closely related to the presence of uncomplexed pyridines in the polymer backbone, and a dipole-dipole relaxation is most likely responsible for it. To investigate whether or not the time stability of the nonlinearity is related to the pyridine moieties in 1, we have investigated the NLO properties of 3, a related copolymer where all unbounded pyridines are substituted by benzene. The decay rate of the SHG signal is shown in Figure 3. A significant improvement is achieved, and the value of the decay constant k expressed as $d_{33}/d_{33(t=0)} = Ae^{-tk}$ is 10 days. We have checked that the stability over time of a poled copolymer (90% styrene-10% vinylpyridine) free of tungsten in which pyridines are pushed further apart from one another could exceed several hours, which definitely supports the role of these mobile organic dipoles in the relaxation process.

Conclusion

To date, the most widely practiced method to engineer molecules into acentric arrangements is the poled polymer approach. In this method, the bulk properties do not arise from β only but also from the $N\mu\beta$ product. Although most of the common organic chromophores used in poled polymers have large μ values, this is not

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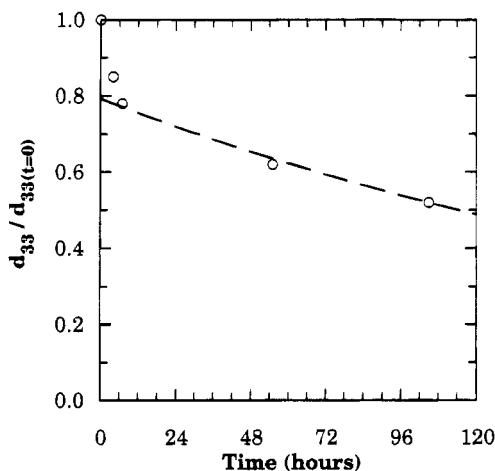


Figure 3. Decay rate of polymer **3** containing 1 W(CO)₅/18 styrenes. The data were recorded after an initial 15 min. The dotted line is the curve $d_{33}/d_{33}(t=0) = Ae^{-t/k}$ obtained for $k = 11$ days which does not take into account the fast initial decay.

the case for (CO)₅W-(substituted pyridine), where the withdrawing effect of the substituent increases the absolute β value but lowers the dipole moment. The solubility of the polymers containing tungsten and the yields of the syntheses were found to decrease dramatically when increasing the functionalization level. It was

never possible to functionalize more than 25% of the pyridine units, and the glass transition temperatures of the resulting polymers were found to increase unexpectedly. In addition, experiments carried out at 70 °C on polymers exhibiting glass transition temperatures up to 110–120 °C induced quite inefficient poling, and heating the (CO)₅W containing polymers for several hours at 120 °C were shown to result in a decomposition of the chromophores.

4-Poly(vinylpyridine) and related Lewis base copolymers appear to be very versatile host structures. They offer convenient linkage to many inorganic and organometallic species. However, unbonded pyridine units have a dramatic effect on the temporal stability of the poled polymers which should be either copolymerized with an apolar monomer (e.g., styrene) or highly functionalized. One of the most interesting aspect of the poly(vinylpyridine) polymer is related to the surprisingly fast relaxation of the pyridine moieties, which could be used as probes toward theoretical data about the guest chromophores such as molecular mobility or the sign of β .

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