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**New Organometallic Polymeric Materials: The
Search for $\chi^{(2)}$ NLO Organometallic Polymers**

by

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New Organometallic Polymeric Materials: The Search for $\chi^{(2)}$ NLO Organometallic Polymers

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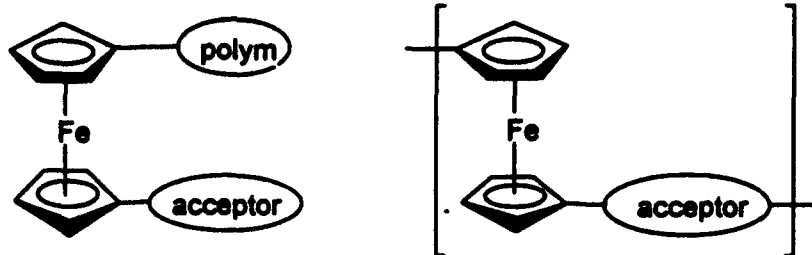
A brief overview of organometallic $\chi^{(2)}$ nonlinear optical (NLO) polymers is presented. The synthesis of new ferrocene NLO-phores is presented along with their copolymerization with methyl methacrylate to generate organometallic NLO-polymers (NLOPs). A new class of organometallic NLO-phores were synthesized by condensation of ferrocene-carboxaldehyde with fluorene compounds. The fluorenyl-ferrocene NLO-phores displayed interesting linear optical properties and reactivity. NLO-spectroscopy was employed to study the orientation and relaxation behavior of the new organometallic NLOPs and we report on these interesting results.

Introduction

Transition metal containing polymeric materials represents an important and active area of materials research.¹ Ferrocene containing polymers have been utilized in a broad range of applications, ranging from batteries² to NLO materials.³ Ferrocene has long been recognized to stabilize alpha-carbocations⁴ and can serve as an excellent electron-donor for an NLO-phore.⁵ Our program has focused on the incorporation of ferrocene based NLO-phores into polymeric materials using covalent bonds.⁶ To our knowledge, the ferrocenyl NLOPs presented below, are the only $\chi^{(2)}$ organometallic NLOPs reported in the literature. Only the side-chain organometallic NLOPs have been demonstrated to show second harmonic generation (SHG) after alignment by corona poling.⁶

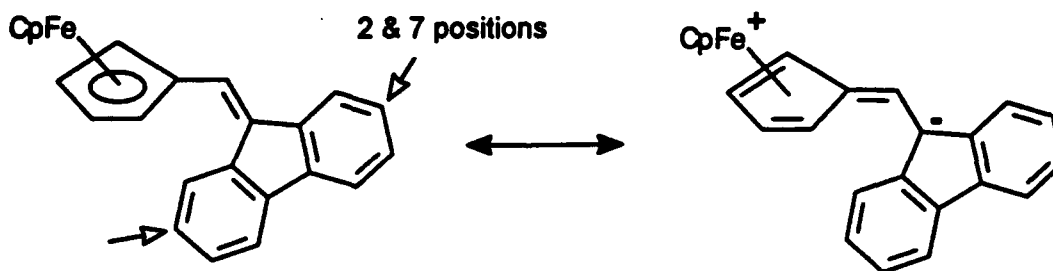
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We envisioned that fluorenyl-ferrocenes, as depicted below, would be an interesting new class of NLO-phores. With the placement of electron-withdrawing groups at the 2 and 7-positions the complexes would model the λ -organic NLO-phores designed by Watanabe and coworkers.⁷ Subsequent incorporation into a polymer backbone would give rise to an "accordion" NLO polymeric material with alternating apexes fixed.⁶ In principle, this should facilitate the alignment process by predisposing part of the polymer backbone into the desired orientation.

In the cartoon below the resonance structure on the right sacrifices one "cyclopentadienyl anion" to generate the fluorenyl carbanion; hence, there should be little net loss in aromaticity. This "no net loss of aromaticity" has recently been exploited by Marder and coworkers in designing NLO-phores with large hyperpolarizabilities.⁹

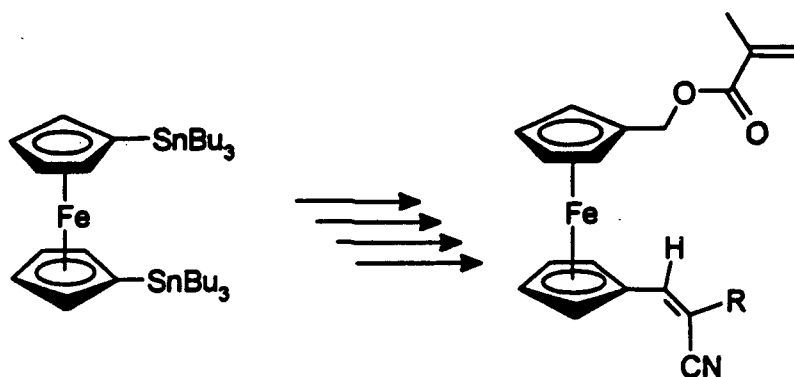


In this paper we will discuss the synthesis and characterization of ferrocene based NLOPs and a study of their orientation and relaxation behavior using NLO-spectroscopy.¹⁰ Included in this work is the synthesis of a new class of fluorenyl-ferrocene NLO-phores and a detailed study of their chemistry and the linear optical properties of the new NLO-phores. The fluorenyl-ferrocene NLO-phore/monomer was successfully incorporated in the backbone of a conjugated organic polymer.

Results & Discussion

Monomer Synthesis & Structural Analysis. We have prepared a variety of vinyl-ferrocene NLO-phores (Scheme 1). The synthetic routes utilize the selective and efficient functionalization of the cyclopentadienyl rings developed in our laboratory.¹¹ We found through structural analysis for a series of complexes that the orientation of the vinyl moiety is apparently controlled (planar for strong electron acceptors) by the nature of the substituent.¹² We have not observed bond averaging for these organometallic systems as seen in certain organic NLO-phores where strong ground state interaction of acceptor and donor has been proposed.¹³ The vinyl-ferrocene NLO-phores display λ_{max} of around 480 nm; thus, one has to be cognizant of resonance enhancement in measurements using the second harmonic generation signal while employing a fundamental laser source of 1064 nm.

Scheme 1



1a, R = CN

1b, R = CO₂Et

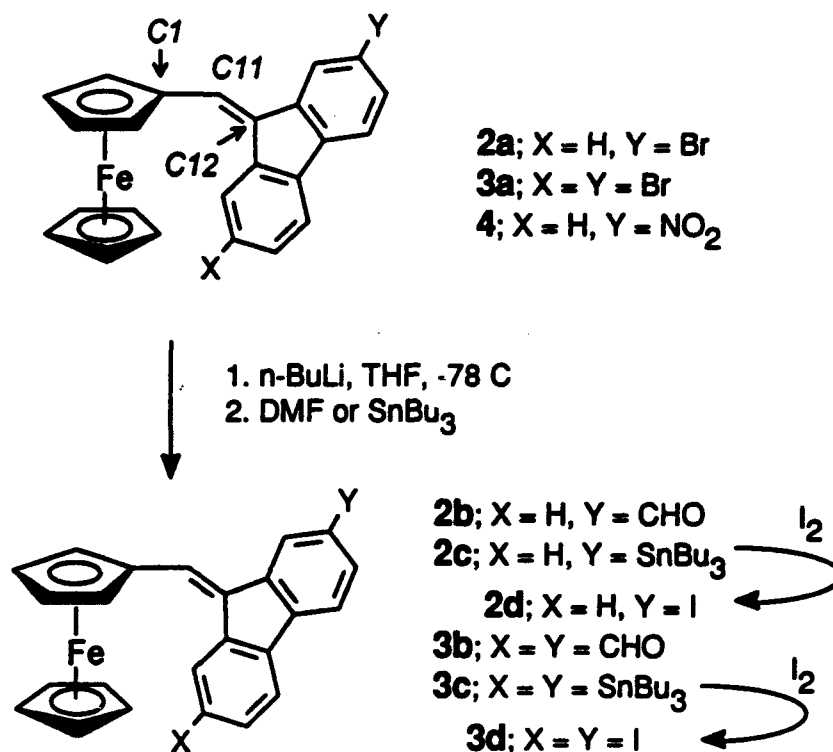
1c, R = 4-bromophenyl

1d, R = 4-pyridyl

The fluorenyl-ferrocene based NLO-phores have been prepared by condensing 2-bromo-, 2,7-dibromofluorene, and 2-nitrofluorene with ferrocene carboxaldehyde to afford 2a, 3a, and 4, respectively, all in reasonable yield.¹⁴ For 2-nitrofluorene the base used is potassium *tert*-butoxide and for the bromofluorenes, lithium diisopropylamide (LDA). Complexes 2a and 3a undergo clean halogen-metal exchange by treatment with *n*-BuLi in tetrahydrofuran (THF) at -78 °C and are then converted to their respective carboxaldehyde¹⁵ and tributylstannyl¹⁶ derivatives by

treatment with DMF and Bu_3SnCl , respectively, in moderate yield (Scheme 2). Oxidative cleavage of the aryl-tin bond¹⁷ with I_2 affords the *mono*- and *bis*(iodo) complexes in good yield (Scheme 2).

Scheme 2



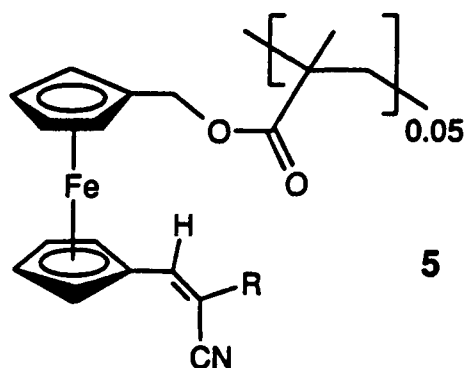
A structural study was initiated to determine the orientation of the fluorenyl-ring and possibly reveal any bond distortions (*i.e.* bond alteration or averaging). Single-crystal x-ray molecular structures were completed for complexes 2b and 3b. A detailed account of the crystallographic study for both structures is presented elsewhere.¹⁸ The fluorenyl-ring system is $39 (\pm 1^\circ)$ degrees out of plane with the $\eta^5\text{-C}_5\text{H}_4$ ring in both complexes. This is different from what we have observed previously in the vinyl-ferrocene systems discussed above where the substituent appeared to control planarity of the system.¹² The *exo*-double bond (C11-C12) is distorted from planarity by 7-9 degrees (defined by C13-C12-C11-C1). The two structures do not show significant differences in their C1-C11 and C11-C12 bond distances [2b, 1.450(6), 1.354(6); 3b, 1.458(3), 1.340(3); respectively]. We would anticipate that contribution of a dipolar structure to the ground-state configuration would lead to a shortening of the C(1)-C(11) bond and lengthening of the C(11)-C(12) bond.

We tested for solvatochromism in the new fluorenyl-ferrocene NLO-phores. The data is presented in Table I. It is quite evident that the electron-withdrawing groups have an effect on the metal to ligand charge transfer (MLCT) band.¹⁹ These data imply that there is indeed a meaningful interaction between the iron center and the fluorenyl-ring system. The observation of a solvatochromic effect for **4** (hexane $\Rightarrow$ CH₂Cl₂, red-shift of 20 nm) is consistent with a dipolar excited state. It is worth noting that the change in dipole moment ($\mu_{\text{ground-state}} - \mu_{\text{excited state}}$), which is often indicated by a solvatochromic shift, can be used to estimate the hyperpolarizability of a given material.²⁰

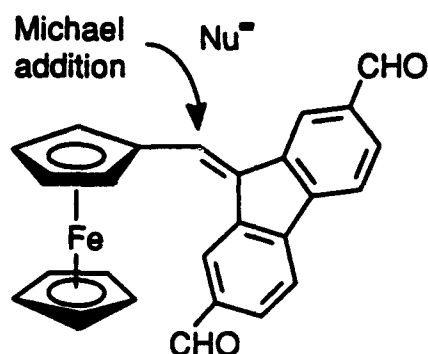
Table I. Linear Optical Data For Selected NLO-phores.

Compound	Solvent	λ_{max} (nm) [$\epsilon \times 10^3$]
3a	CH ₂ Cl ₂	502 [3.01]
3b	CH ₂ Cl ₂	522 [6.50]
4	CH ₂ Cl ₂	512 [6.76]
	EtOH	506
	hexanes	492

Monomer Reactivity and Polymer Synthesis. Monomers **1a-d** were copolymerized with methyl methacrylate (MMA) by free-radical initiation. The monomers were incorporated into the copolymers **5** at the same level as the feed-stock ratio of ferrocenyl monomer/MMA. The copolymers each had an identical λ_{max} as the respective starting monomer, indicating the NLO-phore was indeed intact.

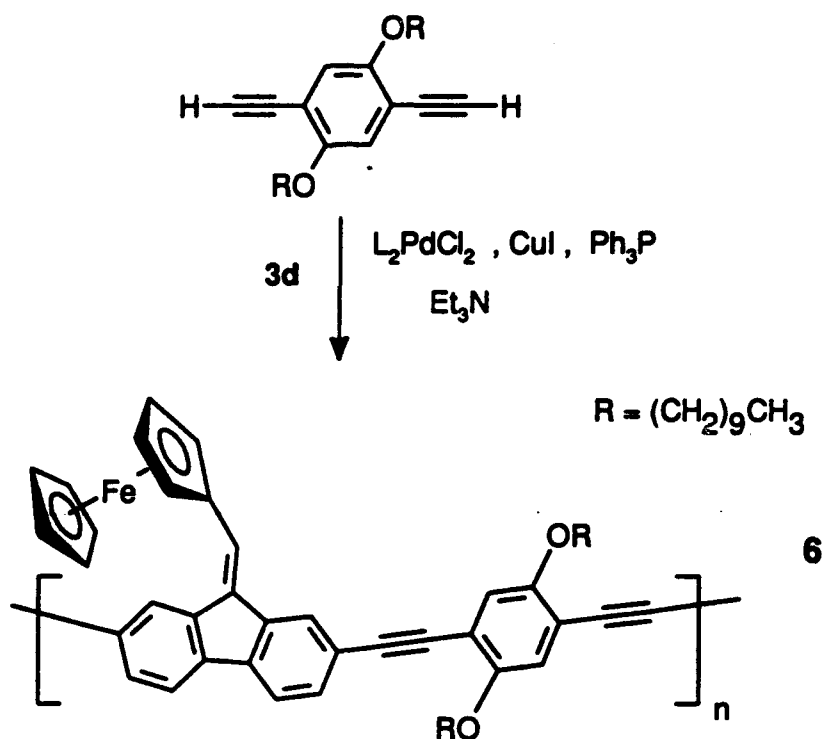


By analogy with our recent success in preparing ferrocenyl polymers via a Knoevenagel polycondensation²¹ we treated **3b** with a bis(cyanoacetate) comonomer. To our surprise, regardless of the base employed, the reaction afforded a complicated mixture of products, none of which displayed the expected and distinctive cyanocinnamate vinyl proton resonance.²² A model study using **3b** and ethyl cyanoacetate again gave a complicated mixture of products. The product-mixture is yellow and this is suggestive that some type of reaction is occurring which breaks conjugation between the fluorenyl and Cp rings. Michael-addition at the C(11) vinyl carbon would represent such an event.



The palladium catalyzed cross-coupling of **3a** with phenylacetylene was found to lead to decomposition of the acetylene and recovery of **3a**.²³ In another model study we employed **3c** in the Stille cross-coupling reaction with acid chlorides²⁴ and found the reaction led to the formation of ketone, but also several additional by-products. With so many side-reactions we deemed the reaction unsuitable for polymerization studies. We did find that the iodo derivatives undergo facile palladium/copper catalyzed alkynylation and were successful in preparing copolymer **6** (Scheme 3).²⁵ Copolymer **6** was produced in high yield and purity [M_n = 67,000, polydispersity 3.8].

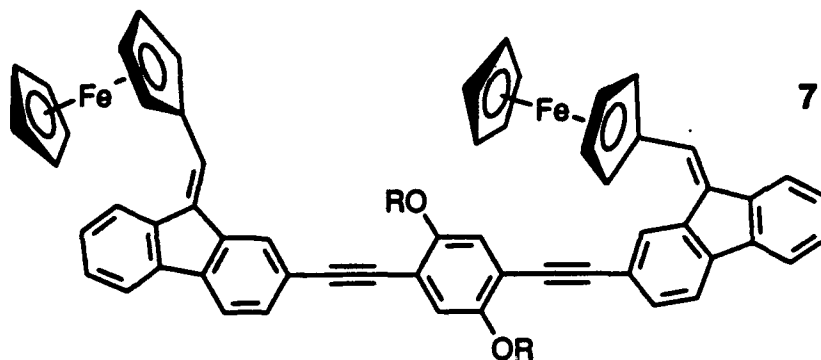
Scheme 3



In some polymerization runs the alkyne comonomer underwent slight decomposition, producing imbalanced stoichiometry, which in turn produced a low molecular weight polymer with fluorenyl-iodide end-caps [$M_n = 7000$, average degree of polymerization = 10]. Copolymer 6 was soluble in common organic solvents and cast very tough, free-standing films.

The thermal behavior and stability of copolymer 6 was measured using TGA and DSC. In the DSC scan we observe a small endothermic transition ($\sim 80^\circ\text{C}$, possibly a melting-point), then an exothermic event ($\sim 175^\circ\text{C}$), and finally an endothermic event beginning at 275°C . The middle event is likely some type of organizational process (*e.g.* crystallization).²⁶ Stopping the DSC scan at 250°C , cooling the sample, and then reheating the sample showed no endo- or exothermic events below 250°C . A film of 6 was heated under nitrogen and viewed using a polarizing microscope. We did not observe any apparent phase transitions from 40 to 200°C . An endothermic event, which began at $\sim 275^\circ\text{C}$, was concomitant with a significant weight loss in the TGA. The loss in mass corresponds to removal of two decyl groups per repeating unit. A film of 6 was cast on a sodium chloride plate and infrared spectra were obtained before and after heating the sample to 400°C for 30 min. The infrared spectrum after heating does not indicate quinone formation (*i.e.* $\text{C}=\text{O}$ stretch), but is supportive of the ferrocene-fluorenyl remaining intact.

We prepared the model compound **7** by cross-coupling **3d** with 1,4-bis(ethynyl)-2,5-bis(decoxy)benzene. Complex **7** is isolated as an orange oil and displays spectroscopic data very similar to copolymer **6**. Cyclic voltammetry of complex **7** shows two reversible oxidation events, one at +0.11 V (two-electron event) and another at +0.71 V (one-electron, peaks relative to the ferrocene/ferrocenium couple). We interpret this to be oxidation of the ferrocenyl²⁷ units (uncoupled events) followed by a more difficult oxidation of the hydroquinone moiety. Surprisingly, copolymer **6** (low molecular sample, $M_n = \sim 7,000$) shows *only a single* and very reversible oxidation event at +0.13 V. Could an extended array of ferrocenium ions be oriented in such manner as to "protect" the hydroquinone polymer backbone from further oxidation? This is an intriguing result and deserves further investigation.



Orientation and Relaxation Studies For the Organometallic Polymers Using Second Harmonic Generation (SHG). Initial experiments were conducted to determine the optimum conditions for observing SHG for copolymers **5**. Only copolymer **5d** did not show any SHG activity after corona poling at T_g plus 25 °C. Polymers **5a** and **5c** displayed the highest SHG signals when poling temperatures of T_g plus 25 °C are employed. In this temperature region the polymer is mobile enough to allow the NLO-phores to readily orient into the required noncentrosymmetric macroscopic structure, yet the temperature is generally not excessive to degrade the polymer or have electric field effects dominate.²⁸ It is also important to note that second order susceptibility is inversely proportional to temperature.²⁹

The polymers are poled at T_g plus 25 °C for 20 min and then allowed to cool to ambient temperature with the electric field still applied. Upon reaching ambient temperature, the voltage is removed, and decay of the SHG signal is monitored. The decay of $\chi^{(2)}$ over time for **5c** is shown

in Figure 1. The decay data following the removal of the electric field was not successfully fit using the Williams-Watt stretched exponential. The WW fit indicated too slow a relaxation process at short times and too fast a relaxation process at long times for both systems. An alternative biexponential fit, $y = \theta_1 \exp(-t/\tau_1) + \theta_2 \exp(-t/\tau_2)$, was used to fit the data, and is represented as a solid line in the Figures. This equation is based on fitting parameters which do not have direct physical significance for describing relaxation behavior but can be used to illustrate a "short-time" and "long-time" relaxation.

It appears that packing of the polymer chains is the dominant effect in the orientation and relaxation behavior of the organometallic NLO-phore. Packing appears to be dependent not only upon NLO-phore structure, but also the age of the polymer films. Interestingly, the smaller NLO-phore (*i.e.* in 5a) shows a lower initial SHG signal; however, better long term stability in comparison to the larger NLO-phore in 5c. Polymer 5a exhibiting observable signal for hours as opposed to seconds for 5c. This marked difference in behavior of $\chi^{(2)}$ for the two systems may be rationalized with molecular packing arguments. The polymer chains which pack more efficiently may provide a more stable microenvironment for the NLO-phores than those chains which are not packed as densely. Since densely packed chains exhibit less segmental mobility relative to unpacked chains, those NLO-phores that have been oriented by the electric field would be more likely to retain their orientation.

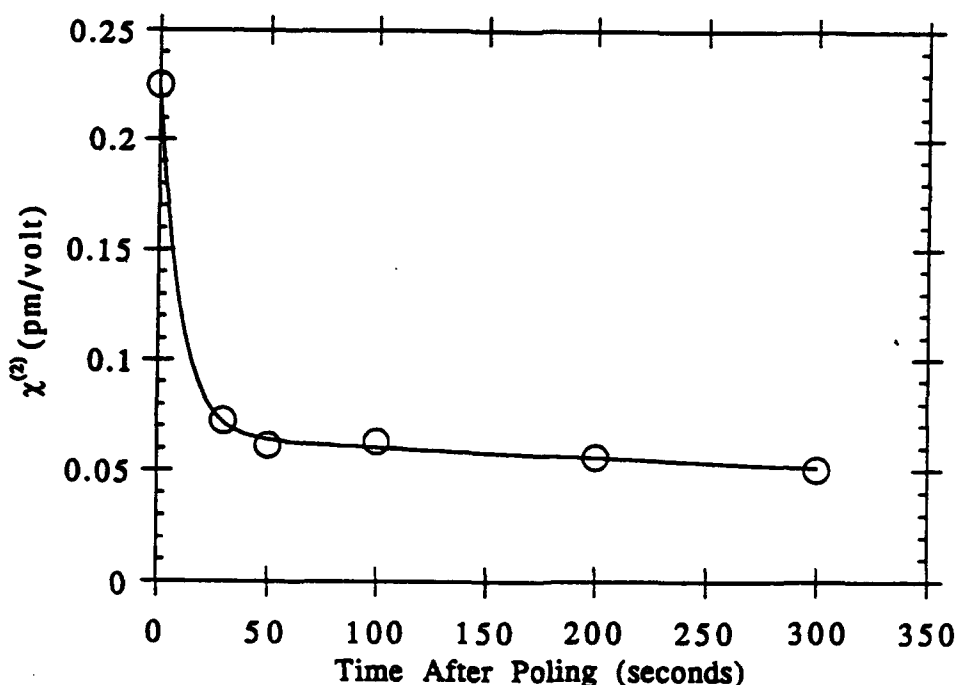


Figure 1. Long term Stability of $\chi^{(2)}$ for copolymer 5c. Solid line indicates biexponential fit with fitting parameters $\theta_1=0.16$, $\tau_1=10$ s; $\theta_2=0.07$, $\tau_2=1231$ s.

Support for the packing argument is found in experiments where the aging of the polymer films is erased by maintaining the films at temperatures well above the T_g for a period of time (at least 1 h) before the poling process is commenced. If the packing argument is correct, then the $\chi^{(2)}$ signal should be less stable and also exhibit a larger initial value. It can be seen in Figure 2 that indeed for both polymers the initial magnitude of the SHG signal is greater and the rate of decay for the signal is increased, particularly so in the case of 5c.

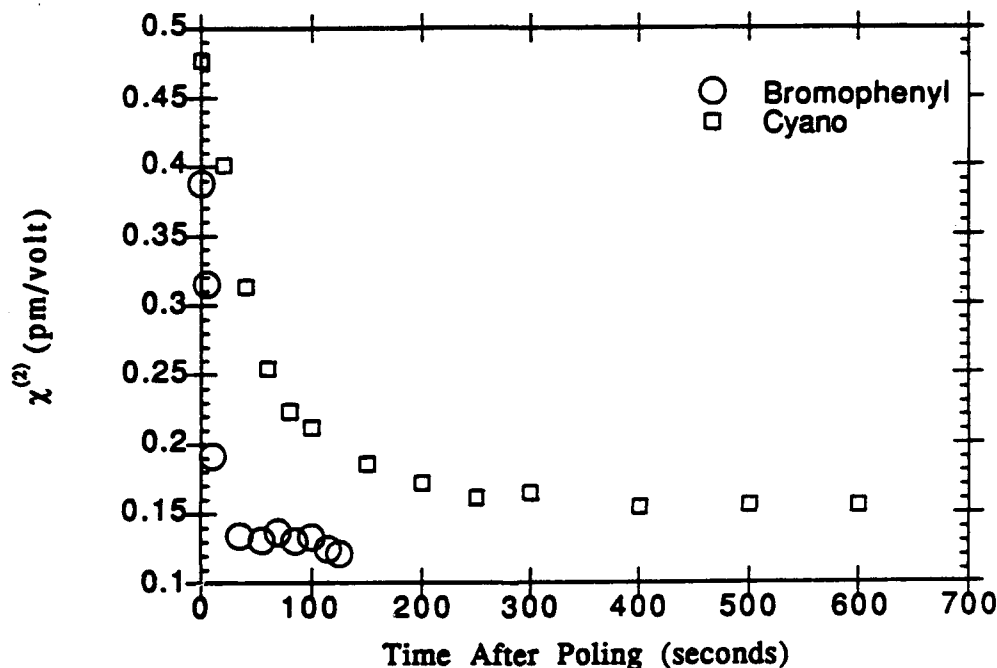


Figure 2. Stability of $\chi^{(2)}$ for copolymers 5c (O) and 5a (□) following erasure of thermal history.

Concluding Remarks

Our work in the area of organometallic NLO polymers demonstrates the feasibility of preparing organometallic NLOPs and that NLO-spectroscopy is a useful tool for probing the orientational and relaxation behavior of the organometallic NLO-phores. By varying the structure of the organometallic NLO-phore we were able to determine that packing of the organometallic NLO-phore within the polymer matrix is very important and was shown to in at least one case, dominate size considerations. Physical aging of the polymer films led to a reversible densification of the polymer matrix. The aged polymer films showed a greater resistance to alignment with a concomitant increase in the ability to retain NLO-phore alignment. These data are consistent with a packing argument.

Erasure of the thermal history of aged films by heating prior to poling also supported the idea of tight packing through densification.

Studies are continuing involving the synthesis and evaluation of organometallic NLO-polymers and super-macromolecular organometallic assemblies.

Selected Experimental³⁰

SHG Measurements. A Continuum NY61-10 Q-switched Nd:YAG laser generated p-polarized light at 1.064 μm . The fundamental beam was split so the sample and a y-cut quartz reference could be tested simultaneously, and lenses were used to vary the size and intensity of the laser beam impinging on the sample. Lenses were placed directly behind the sample and reference to focus the frequency doubled light through infrared filters, insuring that only 532 nm light passed into the monochromator and photomultiplier tube (PMT). The PMT signal was sent to a gated integrator and boxcar averager. A Sparc IPC work station was used to collect and store data. The sample was vertically mounted on a temperature-controlled copper block so that the laser beam struck the sample at a 68° angle relative to the normal of the sample. Samples were poled using a corona discharge generated by a tungsten needle across a 1 cm air gap. The corona current was limited to 3 μA to prevent damaging the sample.

SHG Sample Preparation. The polymer samples were dissolved in spectrophotonic grade chloroform (Mallinckrodt) to produce solutions with 10% polymer by weight. Solutions were filtered (5 μm) and then spun cast onto indium tin oxide (ITO) glass substrates. Film thicknesses varied from 2 to 6 μm (± 0.5) thick, as measured by diamond stylus profilometry. Films were carefully dried to remove any excess solvent.

$\{\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{O}_2\text{CC}(\text{CH}_3)=\text{CH}_2\}\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{C}(\text{CN})_2\}$ (1a, R = CN). ^1H NMR (CDCl_3) δ 7.68 (s, 1 H, =CH), 6.14 (s, 1 H, =CH₂), 5.62 (s, 1 H, =CH₂), 4.97 (t, J = 2 Hz, 2 H, Cp), 4.86 (s, 2 H, CH₂O), 4.81 (t, J = 2 Hz, 2 H, Cp), 4.40 (t, J = 2 Hz, 2 H, Cp), 4.34 (t, J = 2 Hz, 2 H, Cp), 1.96 (s, 3 H, CH₃); ^{13}C NMR (CDCl_3) δ 166.9 (CH₂O₂C), 162.7 (=CH), 136.0 (=CMe), 114.7 (C=N), 114.0 (C=N), 85.2 (=C(CN)₂), 75.6 (Cp CH), 72.1 (Cp CH), 71.4 (Cp CH), 61.4 (CH₂O), 18.3 (CH₃); IR (CH₂Cl₂) $\nu_{\text{C=N}}$ 2226 cm^{-1} ; UV-vis (CH₂Cl₂) λ_{max} = 526 nm (ϵ = 2.99×10^3). Anal. Calcd for C₁₉H₁₆FeN₂O₂: C, 63.36; H, 4.48; N, 7.78. Found: C, 63.10; H, 4.60; N, 7.50.

Preparation of $\{\eta^5\text{-C}_5\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{CH}=[9\text{-(2,7-bis(iodo)fluorenyl)}]\}$ (3d). A chilled (0 °C) THF (40 mL) solution of 2d (1.0 g, 1.1 mmol) was treated with I₂ (0.54 g, 2.1 mmol). The solution was allowed to react at 0 °C for 30 min and then diluted with ether (40 mL). The organic layer was

washed with 10% Na₂SO₃ (2 x 40 mL), brine (40 mL), and then dried over K₂CO₃. The solvents were removed under reduced pressure and the crude product was crystallized from ether/hexanes to give pure **3d** (0.31 g, 48%); ¹H NMR (CDCl₃) δ 8.60 (s, 1 H, Ar CH), 8.08 (s, 1 H, Ar CH), 7.69-7.64 (m, 2 H, Ar CH), 7.47-7.43 (m, 3 H, Ar and vinyl CH's), 4.71 (t, *J* = 1.9 Hz, 2 H, Cp CH), 4.56 (t, *J* = 1.8 Hz, 2 H, Cp CH), 4.25 (s, 5 H, Cp CH); ¹³C NMR (CDCl₃) δ 141.5, 138.8, 138.4 (Ar C), 136.5, 136.3, 135.9, 132.9, 130.8, 129.6, 128.7, 121.3 (vinyl and Ar CH's), 80.1 (*ipso*-Cp), 71.0, 70.6 (Cp CH's), 69.7 (Cp CH's); UV-vis (CH₂Cl₂) λ_{max} = 502 nm (ε = 3.29 x 10³). Anal. Calcd for C₂₄H₁₆FeI₂: C, 46.94; H, 2.63%. Found: C, 47.50; H, 2.72%.

Preparation of {η⁵-C₅H₅}Fe{η⁵-C₅H₄CH=[9-(2-nitrofluorenyl)]} (4**).**

One equivalent of 2-nitrofluorene (0.99 g, 4.7 mmol) was added to a solution of ferrocenecarboxaldehyde (1.0 g, 4.7 mmol) in THF (100 mL) at room temperature. Two mol-equiv of potassium *t*-butoxide (1.1 g, 9.4 mmol) were added and the mixture was stirred for 15 min. The mixture was then diluted with ether (100 mL) and run through a flash column (deactivated Al₂O₃, 1 cm) to remove a heavy black precipitate. The resulting solution was further diluted with ether (50 mL), washed with water (2 x 100 mL), then brine (100 mL), and dried over K₂CO₃. The crude product was subjected to column chromatography (2 x 15 cm) on deactivated alumina. Elution with EtOAc/hexanes (1/20, v/v) gave two major bands, the first was a dark purple band and this was found to be pure **4** (0.38 g, 20%, mp > 300°C). ¹H NMR (CDCl₃) δ 9.16 (s, 1 H, Ar CH), 8.64 (s, 1 H, Ar CH), 8.31-8.22 (m, 2 H, Ar CH), 7.88-7.81 (m, 2 H, Ar or vinyl CH), 7.65-7.63 (m, 1 H, Ar or vinyl CH), 7.46-7.33 (m, 2 H, Ar CH), 4.78-4.76 (m, 2 H, Cp CH's), 4.61 (t, *J* = 1.8 Hz, 1 H, Cp CH's), 4.56 (t, *J* = 1.8 Hz, 1 H, Cp CH's), 4.25 (s, 5 H, Cp CH's); ¹³C NMR (CDCl₃) δ 146.9, 146.6, 145.8, 143.3, 141.5, 140.5, 138.4, 138.2, 137.1, 135.8 (aromatic C), 131.3, 130.4, 130.1, 128.7, 128.5, 128.1, 127.6, 124.3, 122.9, 122.5, 121.0, 120.9, 119.8, 119.5, 115.1 (aromatic or vinyl CH's), 80.2, 79.9 (*ipso*-Cp) 71.1, 71.0, 70.6 (Cp CH's), 69.7 (Cp CH's). UV-vis (CH₂Cl₂) λ_{max} = 512 nm (ε = 6.76 x 10³).

PMMA Copolymer **5 (R = CN).** A Schlenk flask was charged with benzene (3 mL), **1a** (0.34 g, 0.95 mmol), methyl methacrylate (2.02 mL, 18.9 mmol), and AIBN. The mixture was heated to reflux for 8 h and the solvent removed under reduced pressure. The polymer was redissolved (~1.3 g did not dissolve) in chloroform and precipitated into methanol (0.55 g, 25%). ¹H NMR (CDCl₃) δ 7.73 (br s, 1 H, =CH), 4.99 (t, *J* = 2 Hz, 2 H, Cp), 4.84 (t, *J* = 2 Hz, 2 H, Cp), 4.70 (s, 2 H, CH₂), 4.37 (m, 4 H, Cp), 3.58 (s, PMMA OCH₃), 1.92 (br s, 2 H, PMMA CH₂), 1.79 (br s, 2 H, CH₂), 1.00 (s, PMMA CH₃), 0.82 (s, 3 H, CH₃). Anal. Calcd: N, 1.24. Found: N, 1.21.

Preparation of Polymer **6.** A 25 mL Schlenk tube was charged with **3d**

(70 mg, 0.11 mmol), 1,4-bis(decoxy)-2,5-diethynylbenzene (53 mg, 0.12 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (2 mg, 3 mol-%), CuI (1 mg, 6 mol-%), PPh_3 (2 mg, 6 mol-%), and triethylamine (5 mL) under nitrogen. The mixture was warmed to 50 °C with stirring for 2 h and then diluted with dichloromethane (100 mL). The organic layer was washed with 10% NaCN (100 mL), water (2 x 100 mL), brine (100 mL), and then dried over K_2CO_3 . The solvents were removed and the polymer washed with ether (5 mL) and then dried under reduced pressure at 65 °C for 24 h (53 mg, 61%). ^1H NMR (CDCl_3) δ 8.49-8.46 (br s, 1 H, Ar CH), 8.01-7.97 (br s, 1 H, Ar CH), 7.76-7.72 (m, 2 H, Ar CH), 7.61-7.54 (m, 3 H, Ar CH), 7.12, 7.09, 7.06, 7.02 (4 br s, 2 H, Ar CH), 4.80-4.78 (m, 2 H, Cp CH), 4.59-4.55 (m, 2 H, Cp CH), 4.26 (br s, 5 H, Cp CH), 4.14-4.03 (m, 4 H, CH_2O -), 1.95-1.84 (m, 4 H, CH_2 's), 1.61-1.51 and 1.31-1.23 (2 m's, 28 H, CH_2 's), 0.85-0.83 (m, 6 H, CH_3 's). IR (CH_2Cl_2) (alkyne) ν 2206 cm^{-1} ; UV-vis (CH_2Cl_2) $\lambda_{\text{max}} = 514 \text{ nm}$ ($\epsilon = 5.39 \times 10^3$). Anal. Calcd for $[\text{C}_{58}\text{H}_{64}\text{FeO}_2]_n$: C, 81.39; H, 7.59%. Found: C, 79.42; H, 7.72%.

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