also comparable with heterogeneous benzene hydrogenation catalyzed by 0.1 wt % Rh (derived from $RhCl_3$) on silica with a turnover frequency of approximately 10^{-3} molecules of benzene/(surface Rh atom s).[7] The most notable feature of these graphs is that the hydrogenation of toluene continued well past the time at which all the $[(1,5\text{-COD})RhH]_4$ had been consumed. From these data it appears that the hydrogenation reaction was not stoichiometric in Rh concentration, and $[(1,5\text{-COD})RhH]_4$ derived solutions were capable of at least 127 turnovers, after which the experiment was stopped. The compound $[(1,5\text{-COD})RhH]_4$ may be responsible for some catalytic hydrogenation. If it were not an active catalyst, the rate of toluene hydrogenation should increase as the active catalyst is formed and then become constant after all the $[(1,5\text{-COD})RhH]_4$ is consumed. Qualitatively, this appears not to be the case, but the data are not unambiguous in this respect. However, this species must be a precursor to an active hydrogenation catalyst since the hydrogenation activity continues long after the $[(1,5\text{-COD})RhH]_4$ was reacted.

During addition of hydrogen to $[(1,5\text{-COD})RhH]_4$ solutions, a black solid was precipitated and the initial dark red solution became colorless after 60 min, when all the $[(1,5\text{-COD})RhH]_4$ had been consumed. The black solid was isolated and shown to be comprised of agglomerated ~2-nm-sized particles of crystalline rhodium as determined by transmission electron microscopy, energy-dispersive spectroscopy, and electron diffraction (see Figure 2). X-ray powder diffraction experiments could not distinguish between an amorphous material and crystalline rhodium with a small crystallite size. However, the position (2θ) and width of the X-ray diffraction peaks observed at room temperature were consistent with the presence of 2-nm-sized crystallites. On heating this solid to 400 °C, sharp X-ray diffraction peaks were observed at positions that corresponded to the presence of crystalline rhodium. A particle size of 2 nm corresponds to a turnover frequency of 2.3×10^{-3} molecules of toluene/(*surface* Rh atom s).

Preliminary studies of the hydrogenation activity of functionalized aromatic hydrocarbons exhibited quite different behavior. Pyridine-d_5 was not hydrogenated on the same time scale that hydrogenation of benzene-d_6 and toluene-d_8 was observed, but instead, D/H exchange was observed selectively into the *o*-phenyl position as determined by ^{1}H NMR spectroscopy. Furthermore, benzophenone (and acetone) did not react on the same time scale as benzene-d_6 and toluene-d_8, although $[(1,5\text{-COD})RhH]_4$ was converted to Rh metal in every case. In a competition experiment, a mixture of benzophenone and toluene were dissolved in a cyclohexane-d_{12} solution of $[(1,5\text{-COD})RhH]_4$. The rate of hydrogenation of toluene was severely depressed under these conditions. No methylcyclohexane was formed after 120 min. This indicated that the benzophenone probably poisoned the catalytically active sites perhaps via coordination of the carbonyl functionality. Coordination of the nitrogen lone pair of pyridine-d_5 to the catalyst might also explain the observed ortho deuterium D/H exchange as a result of their proximity to the active site(s).

The interaction of toluene with condensed metal vapors has been postulated to result in formation of π-toluene complexes.[1,16,17] The species derived from the condensation of Rh vapor into toluene was found to be an active hydrogenation catalyst for the conversion of toluene to methylcyclohexane.[18] An analogous species may be formed as an intermediate in these reactions. Further studies are in progress to determine the stereochemistry and selectivity of hydrogenation of aromatic hydrocarbons with $[(1,5\text{-COD})RhH]_4$ and to develop the strategy of the removal of alkene ligands from metal–organic complexes to liberate small metal clusters under mild conditions.

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Registry No. $LiBEt_3H$, 22560-16-3; $[(1,5\text{-COD})RhCl]_2$, 12092-47-6; $[(1,5\text{-COD})RhH]_4$, 82660-97-7; $LiBEt_3D$, 74540-86-6; $[(1,5\text{-COD})RhD]_4$, 144001-68-3; $C_6D_5H_6CD_3$, 144001-67-2; Rh, 7440-16-6; H_2, 1333-74-0; benzene-d_6, 1076-43-3; cyclohexane-*1,2,3,4,5,6*-d_6, 144001-66-1; toluene-d_8, 2037-26-5; toluene, 108-88-3; methylcyclohexane, 108-87-2; pyridine-d_5, 7291-22-7.

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Poled Polymeric Nonlinear Optical Materials. Exceptional Second Harmonic Generation Temporal Stability of a Chromophore-Functionalized Polyimide

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Rational synthetic approaches to efficient polymeric second-order nonlinear optical materials[1] must address the crucial requirements of maximizing constituent chromophore number densities while achieving and preserving maximum microstructural accentricity. Acceptable thermal environments must ultimately include those of device fabrication as well as prolonged use. To these ends, poled cross-linkable chromophore-functionalized glassy polymers[2,3] and poled matrices based upon cross-linkable

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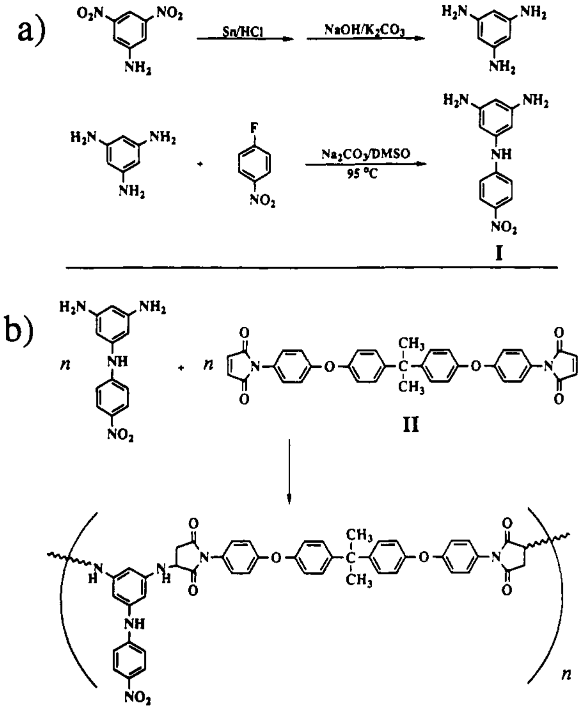
Scheme I



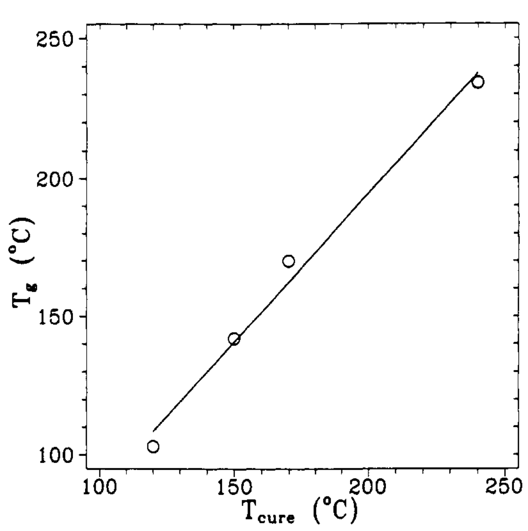


Figure 1. DSC-determined glass transition temperature as a function of polymerization temperature for I-polyimide specimens. Polymerization reactions were carried out at each temperature for 1 h. ○ denotes an experimental data point. The solid line is drawn to aid the eye. T_g's were measured at a heating rate of 10 °C min^{-1}.

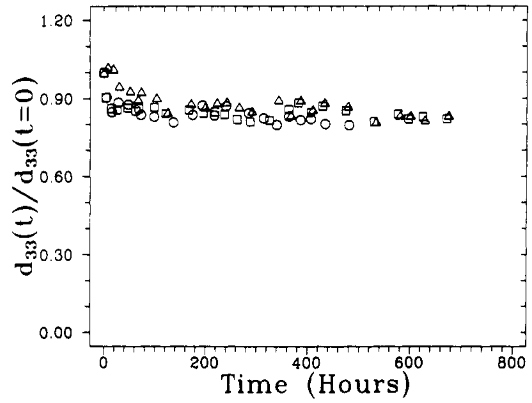


Figure 2. SHG temporal characteristics at 85 °C for three films prepared from reactive NLO chromophore I and bismaleimide II. △, T_{precure} = 100 °C (1 h), T_{cure} = 150 °C; □, T_{precure} = 150 °C (1 h), T_{cure} = 218 °C; ○, T_{precure} = 170 °C (1 h), T_{cure} = 240 °C.

chromophoric co-monomers[4,5] represent significant advances over early guest–host (chromophore-doped) and non-cross-linked systems. Nevertheless, enhancing the limits of materials and SHG thermal/temporal stability remains an important goal. As polymeric materials, polyimides[6] display great structural versatility as well as impressive thermal stability and optical transparency[7] characteristics. Moreover, polyimides have recently been employed as hosts in poled, *guest–host* NLO materials.[8] We report here the first synthesis of an NLO *chromophore-functionalized* poled polyimide and disclose some of the interesting properties of this new material. These include very high T_g values and exceptional SHG temporal stability.

Diamino NLO chromophore I (calculated $\beta_{\text{vec}} = 27.6 \times 10^{-30}$ cm^5 esu^{-1} at $\hbar\omega = 1.17$ eV[9]) was synthesized according to the sequence of Scheme Ia and was characterized by standard spectroscopic and analytical techniques.[10] Films were cast by slow evaporation in a laminar flow clean hood of dry, filtered (5-μm syring filter) THF solutions of I and bismaleimide co-monomer II[11] (~ 1.8 mM in each component) on clean soda lime glass. Partial polymerization (precuring) of the cast films was then achieved by heating at various temperatures in vacuo. Conditions for polym-

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(10) ^{1}H NMR (DMSO-d_6): δ 4.83 (s, 4 H), 5.60 (s, 1 H), 5.69 (s, 2 H), 6.96 (d, 2 H, J = 9.8 Hz), 8.22 (d, 2 H, J = 9.8 Hz), 8.87 (s, 1 H): MS M$^+$ = 244; UV-vis $\lambda_{\max}$ (dioxane) = 417 nm, $\epsilon_{\max}$ = 5080 L mol^{-1} cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.46; H, 4.46; N, 22.90.

(11) Commercially available as BAPP-BMI through Kennedy and Klim, Inc., Little Silver, NJ. We thank Kennedy and Klim for a sample of this reagent.

erization and verification of the type of chemistry[6] portrayed in Scheme Ib were established in solution by ^1H NMR spectroscopy.[12] Cured films were typically 4 μm in thickness as measured by profilometry. Corona poling and final polymerization (curing) of the I-polyimide films was carried out under N_2 at various temperatures for 1.0 h in the in situ SHG instrumentation described previously.[2,4] The corona needle-to-film distance was 1.0 cm and the applied potential was +5.0 to +6.0 kV. Poled films were cooled to room temperature over 0.5 h before removing the poling field, and the initial measurement of storage SHG properties made within 15 min of field removal. SHG measurements on the films (λ = 1.064 μm) were made at room temperature in the p-polarized geometry and were referenced against quartz using procedures and instrumentation detailed elsewhere.[13] Film specimens for time-dependent SHG decay studies were stored in air in a thermostated tube furnace at 85 °C. Films were removed from the furnace and allowed to cool to ambient temperature before SHG measurements were performed. Transmission optical spectroscopic measurements indicated only minor changes in film optical properties through the poling/curing process, arguing for minimal if any thermal decomposition.[14]

In Figure 1 is shown the relationship between the I-polyimide curing temperature and the ultimate, DSC-determined T_g value. The approximate linearity of this relationship is further indication that the polymerization process is well-behaved. The apparent T_g value of 236 °C is to our knowledge, the highest yet reported for a chromophore-functionalized NLO polymer of any type.[1-5,15] Second harmonic indexes, d_{33}, for the poled I-polyimide were found to be in the range (11–13) × 10^{-9} esu. These values are reasonable for a nitroaniline chromophore of the present architecture and estimated matrix chromophore number density ($\sim 7 \times 10^{20}$ cm^{-3}).[1-5] They are comparable in magnitude to d_{33} values of similar chromophore-functionalized NLO polymers.

SHG temporal stability data at 85 °C for three I-polyimide films precured and poled under differing thermal conditions are shown in Figure 2. It was found that increases in the prepoling temperature ($T_{precure}$) are accompanied by increases in the achievable poling temperature (T_{cure}), above which SHG signal loss and film damage are apparent. Importantly, Figure 2 reveals only minor (~ 10–15%) decay in SHG efficiency over the first 24 h at 85 °C and, within the precision of the measurements, *negligible to very minor decay* over the following month at 85 °C. Also noteworthy is the small sensitivity of the $d_{33}(t)$ characteristics to the nature of the precure/cure protocol. Attempts to fit the $d_{33}(t)$ data by nonlinear least-squares methods to either a biexponential[2,4,16] or Kohlrausch-Williams-Watts stretched exponential expression[17,18] were inconclusive (τ values diverged) owing to the small observed d_{33} temporal dependence.

These results demonstrate that NLO chromophore-functionalized polyimide structures can be prepared which, after appropriate thermal polymerization and electric field poling, exhibit very high T_g values, efficient SHG characteristics, and unprecedented SHG temporal stability. Efforts are continuing to further decrease matrix mobility and to introduce higher β chromophores.

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Registry No. I, 143969-94-2; II (copolymer), 143969-95-3; II (SRU), 143969-96-4.

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[12] A solution of I and II in DMSO-d_6 (1:1 stoichiometry, ca. 27 mM in each) was heated at 127 °C and monitored by ^1H NMR until no further changes were observed in the spectra (35 h). During the course of the experiment, resonances at δ = 7.17 and 4.81 disappeared while a resonance appeared at δ = 5.21. These resonances are attributed to the olefinic protons in **II**, the primary amine protons in **I**, and the secondary amine protons in the addition product, respectively. No spectral changes were observed in solutions of **I** or **II** heated alone under the same conditions.

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[14] (a) Films exhibited λ_{max} = 432 nm before precuring, 440 nm after precuring, and 450 nm after poling. Such small shifts in spectra of poled NLO polymers are common and attributable to dichroic,[14b] electrochromic,[14b] and/or interchromophore π–π overlap[14c] effects. (b) Mortazavi, M. A.; Knoesen, A.; Kowel, S. F.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733–741. (c) DiBella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.*, **1992**, *114*, 5842–5849 and references therein.

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[18] $d_{33}(t) = Ae^{(-t/\tau)^\beta}$.

Metamagnetic Properties of a Family of Ferromagnetic Alternating Spin Chains: Bis(dimethylglyoximato)(carboxylato)manganese(III)copper(II)

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The interaction between unpaired electrons are most often of the up–down type. The parallel spin alignment (ferromagnetic interaction) remains exceptional in molecular chemistry and requires the fulfillment of quite peculiar conditions. That is why one of the main challenges in the field of molecular materials is the design of molecular-based ferromagnets[1-4] and several approaches

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