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Thermoset Nonlinear Optical Polymers via Hydrosilation of Chromophores with Tetramethylcyclotetrasiloxane

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ABSTRACT: A new thermosetting matrix for second-order nonlinear optical (NLO) materials based on the hydrosilation reaction of tetramethylcyclotetrasiloxane (TMCTS) with NLO chromophores and dicyclopentadiene is disclosed. Chromophore synthesis, hydrosilation reaction kinetics, processing of prepolymers, and the thermal and second-order optical properties of fully cured films are reported. Thin polymer films (0.5–2.0 μm thick) were spin-cast, precured, and corona-poled while continuing the cure cycle to provide noncentrosymmetric films. The thermal stability of the second-order nonlinearity was measured monitoring the SGH signal as a function of temperature. A formulation comprising dye 7 and TMCTS, which possessed the capability for locking-in the orientation of the chromophore by multisite covalent bonding, maintained a nonlinearity of $d_{31} = 3 \pm 1$ pm/V and demonstrated thermal stability in excess of 190 °C.

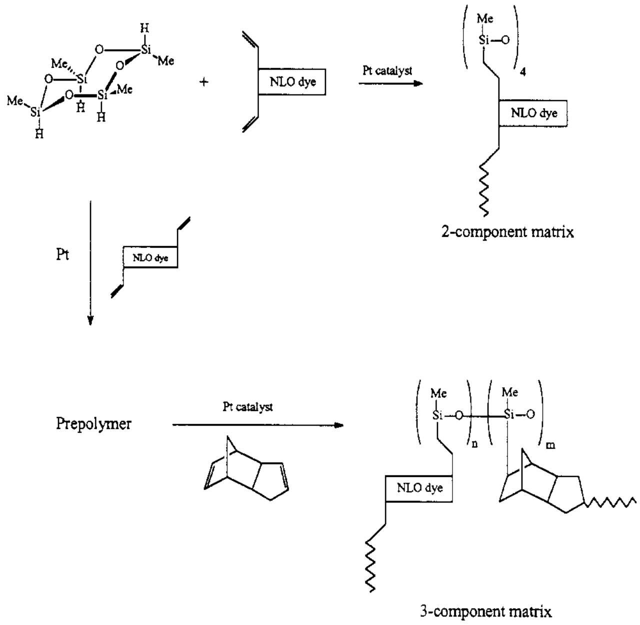
Introduction

Organic polymers comprising dyes with intramolecular charge transfer between a donor and acceptor in a π-conjugated system have been of interest as nonlinear optical (NLO) media.[1] Of particular interest are polymer–dye systems that exhibit high second-order polarization susceptibilities (χ^2) resulting from the unidirectional alignment of charge transfer moieties exhibiting large hyperpolarizabilities (β). Polymer–dye systems can be categorized into four classes: guest/host mixtures, in which the polymer acts as a matrix for a dissolved dye molecule;[2] guest/cross-linked host mixtures, in which the polymer matrix is cross-linked;[3] polymer-bound dyes, wherein the dyes are covalently bonded to a polymer chain;[4] and cross-linked polymer-bound dyes wherein the dyes are covalently bonded to a cross-linked polymer matrix.[5] Recent inquiries into polymeric NLO materials have focused on improving the thermal stability of the second-order optical response of poled, noncentrosymmetric polymers by reducing the mobility of the NLO chromophore in the polymer matrix. Thus, cross-linkable epoxy matrices,[5b,c,e,f] bis- and tris-acrylates,[5a,d] polyurethanes,[5j] photo-cross-linkable cinnamate esters,[5g–i] and thermosetting polyimides[3b] have been investigated in combination with NLO chromophores.

We disclose here a new thermoset matrix for NLO materials based on the hydrosilation reaction of tetramethylcyclotetrasiloxane (TMCTS) with NLO chromophores containing reactive carbon–carbon double bonds and the diolefin cross-linking agent dicyclopentadiene (DCPD) as described in Scheme 1. The thermosetting hydrosilation reaction of cyclic siloxanes and a variety of polyenes has been previously described.[6] The high glass transition temperatures (T_g), optical clarity, and excellent dielectric properties of the cyclic siloxane/polyene thermosets make them attractive candidate for incorporation of NLO chromophores.

We envisioned the possibility of a simple two-component thermoset comprising a polyfunctional NLO chromophore and TMCTS, or a three- or more component system comprising a mono-, di-, or polyfunctional chromophore, TMCTS, and a cross-linking polyene such as dicyclopentadiene to provide additional rigidity to the thermoset matrix. Three distinct types of thermosetting NLO polymers with a decreasing degree of chromophore mobility would be available: type 1, with one covalent bond between chromophore and matrix, would lead to a freely rotating side chain chromophore; type 2, with two covalent bonds participating in the cross-linking reaction from one site on the chromophore π system, would lead to a matrix with restricted rotation of the chromophore (as shown in Scheme 1 for the two-component case); and type 3, with two or more covalent bonds participating in the cross-linking reaction from different sites on the chromophore π system, would effectively lock-in the orientation of the chromophore in the thermosetting matrix (as shown in Scheme 1 for the three-component case). The proper conditions also should provide the capability of forming soluble prepolymers and the potential for a high density of chromophores without the problems inherent in phase separation.

Scheme 1. Thermosetting NLO Polymers via Hydrosilation of Chromophores with TMCTS



Chromophore synthesis, hydrosilation reaction kinetics, processing of prepolymers, and the thermal and second-order optical properties of selected fully cured films are reported.

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Experimental Section

Materials. *N*-Allylanilines were prepared according to the general procedures outlined by Butler et al.[7] Tetramethylcyclotetrasiloxane (TMCTS) was purchased from Hüls Petrarch Systems and purified by fractional distillation. The fraction between 59.4 and 59.7 °C at 50 mmHg was taken. GC analysis of the TMCTS distillate (Varian 6000 gas chromatograph, RTX-1 poly(dimethylsiloxane) column from Restek) showed an area percent purity of 99.7%. HPLC-grade solvents were used as received from Aldrich. The platinum catalyst PC072, which is a platinum divinyltetramethyldisiloxane complex in xylene (3.0–3.5% Pt), was purchased from Hüls Petrarch Systems and diluted tenfold with toluene.

***N*-Allyl-*N*-methyl-4-nitroaniline (1).** *N*-Methyl-4-nitroaniline was alkylated with allyl bromide in the presence of triethylamine and *N*-methyl-2-pyrrolidone (NMP). The crude product was chromatographed (silica) and distilled (110–115 °C, 0.1 mmHg) to give a yellow oil that crystallized upon cooling in a freezer (14.5 g, 75%, mp 37.5–39.5 °C). Recrystallization from methanol gave yellow crystals: mp 38.5–39.2 °C; ^{1}H NMR (CDCl$_3$) δ 8.1 (2H, d, J = 9.3 Hz), 6.62 (2H, d, J = 9.6 Hz), 5.81 (1H, m), 5.18 (2H, m), 4.05 (2H, m), 3.1 (3H, s); IR (KBr) 1595, 1580, 1520, 1485 cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.28. Found: C, 62.49; H, 6.26.

***N,N*-Diallyl-4-nitroaniline (2).** *p*-Fluoronitrobenzene was treated with *N,N*-diallylamine in NMP. The crude oil was distilled (110–120 °C, 0.1 mmHg), chromatographed (silica), and distilled again (100–110 °C, 0.1 mmHg) to give a yellow oil (10.5 g, 48%): ^{1}H NMR (CDCl$_3$) δ 7.95 (2H, d, J = 9 Hz), 6.54 (2H, d, J = 9 Hz), 5.78 (2H, m), 5.1 (4H, m), 3.97 (4H, m); IR (neat) 1595, 1514, 1488 cm^{-1}. Anal. Calcd for $C_{12}N_{14}N_2O_2$: C, 66.04; H, 6.46. Found: C, 66.38; H, 6.55.

***N*-Allyl-*N*-methyl-4-(tricyanovinyl)aniline (3).** *N*-Allyl-*N*-methylaniline was treated with tetracyanoethylene (TCNQ) in pyridine. The crude solid was chromatographed (silica) and recrystallized from ethanol to give **3** as fluffy maroon needles (0.54 g, 54%): mp 155.0 °C; ^{1}H NMR (CDCl$_3$) δ 8.1 (2H, dd, J = 7.3, 2 Hz), 6.7 (2H, dd, J = 7.3, 2 Hz), 5.8 (1H, m), 5.3 (1H, dd, J = 10.3, 1 Hz), 5.2 (1H, dd, J = 17.1, 1 Hz), 4.1 (2H, m), 3.2 (3H, s); IR (KBr) 2215, 1496 cm^{-1}; λ_{max}(CH$_2$Cl$_2$) = 514 nm, ϵ = 23 800 M^{-1} cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.57; H, 4.87. Found: C, 72.41; H, 5.0.

***N,N*-Diallyl-4-(tricyanovinyl)aniline (4).** Diallylaniline was treated with TCNQ in pyridine. Chromatography (silica) of the crude solid gave a red solid that was recrystallize from ethanol to give **4** as red needles (4.1 g, 65%): mp 93–94 °C; ^{1}H NMR (DMSO-d_6) δ 7.8 (2H, d, J = 10 Hz), 6.8 (2H, d, J = 10 Hz), 6.3–5.6 (2H, m), 5.3–5.0 (4H, m), 4.1 (4H, d, J = 6 Hz); IR (KBr) 2220, 1603, 1492 cm^{-1}; λ_{max}(CH$_2$Cl$_2$) = 512 nm, ϵ = 25 600 M^{-1} cm^{-1}. Anal. Calcd from $C_{17}H_{14}N_4$: C, 74.43; H, 5.14. Found: C, 74.32; H, 5.40.

***N,N*-Diallyl-4-[(4′-nitrophenyl)azo]-3-methylaniline (5).** 4-Nitroaniline was diazotized and poured into a mixture of *N,N*-diallyl-3-methylaniline, sodium acetate, and acetic acid. The resulting solid was recrystallized from tetrahydrofuran–ethanol to give **5** (8.0 g, 60%): mp 73–74 °C; ^{1}H NMR (CDCl$_3$) δ 8.3 (2H, d, J = 7.2 Hz), 7.9 (2H, d, J = 7.2 Hz), 7.78 (1H, d, J = 9.9 Hz), 6.58 (2H, s), 5.87 (2H, m), 5.2 (4H, m), 4.02 (4H, m), 2.69 (3H, s); IR (KBr) 1598, 1585, 1510 cm^{-1}. Anal. Calcd for $C_{19}H_{20}N_4O_2$: C, 67.84; H, 5.99. Found: C, 67.57; H, 6.02.

***N,N*-Diallyl-1-amino-4′-nitrostilbene (6).** 4-Nitrophenylacetic acid was treated with (*N,N*-diallylamino)benzaldehyde[8] in piperidine. Recrystallization of the crude solid from methanol gave **6** as bright orange plates (1.8 g, 27%): mp 98–99 °C; ^{1}H NMR (DMSO-d_6) δ 8.1 (2H, d, J = 10 Hz), 7.65 (2H, d, J = 10 Hz), 7.4 (2H, d, J = 10 Hz), 7.25 (1H, s), 7.1 (1H, s), 6.0–5.6 (2H, m), 5.1 (4H, d), 3.95 (4H, m); λ_{max}(CH$_2$Cl$_2$) = 439 nm, ϵ = 32 200 M^{-1} cm^{-1}.

***N,N*-Diallyl-4-[[3-[[2-(2-cyclopentenyl)ethyl]oxy]-4-nitrophenyl]azo]aniline (7).** 5-Fluoro-2-nitrophenol was alkylated with 3-(2-bromoethyl)cyclopentene in methyl ethyl ketone in the presence of potassium carbonate. The resulting oil (7.2 g) comprised 65 mol % of the desired 2-[[2-(2-cyclopentenyl)ethyl]oxy]-4-fluoronitrobenzene by NMR analysis: ^{1}H NMR (CDCl$_3$) δ 7.9 (d of d, 2H), 6.8 (m, 2H), 5.75 (d of m, 2H), 4.12 (t, 2H), 2.9 (m, 1H), 2.4–1.3 (m, 6H).

The above oil was treated with ammonium hydroxide and *N*-methylpyrrolidone. The resulting crude solid was chromatographed (silica) to give 3-[[2-(2-cyclopentenyl)ethyl]oxy]-4-nitroaniline (**8**) as an oil (2.74 g, 38%): ^{1}H NMR (CDCl$_3$) δ 7.9 (d, 1H), 6.2 (d and s, 2H), 5.74 (m, 2H), 4.3 (bs, 1H), 4.07 (t, 2H), 2.93 (m, 1H), 2.33 (m, 2H), 2.1–1.4 (m, 5H).

The nitroaniline **8** was diazotized and poured into a mixture of sodium acetate, acetic acid, and *N,N*-diallyl-*m*-toluidine. Chromatography (silica) gave dye **7** as a red oil (3.0 g, 61%): ^{1}H NMR (CDCl$_3$) δ 7.96 (d, 1H), 7.75 (d, 1H), 7.51 (s, 1H), 7.41 (d, 1H), 6.57 (m, 2H), 5.9–5.7 (m, 4H), 5.24 (m, 4H), 4.25 (t, 2H), 4.03 (m, 4H), 2.93 (m, 1H), 2.69 (s, 3H), 2.35 (m, 2H), 2.1–1.4 (m, 4H).

Hydrosilation Kinetics. The following example illustrates the procedure used to determine the kinetics of the hydrosilylation reaction. Into a dried 25-mL round-bottom flask were added *N*-methyl-*N*-allyl-4-nitroaniline (0.96 g, 5.0 mmol, 5.0 mequiv of olefin), TMCTS (0.60 g, 2.51 mmol, 10.0 mequiv of SiH), and toluene (0.68 g). The flask was fitted with a reflux condenser and magnetic stirrer and then purged with argon for 10 min while warming in a 65 °C oil bath. After warming to 65 °C, the flow of argon was stopped and 61 μL of catalyst solution was added (100 ppm Pt relative to total weight of solid). Aliquots of ca. 0.35 mL were removed from the flask at 1-h intervals after the addition of the catalyst. These aliquots were immediately quenched with 4 drops of a 0.1% (wt/wt) solution of 1,2-bis(diphenylphosphino)ethane dissolved in chloroform. After all samples were collected, they were placed on a vacuum line for 2 h to remove toluene. After redissolving in CDCl$_3$, ^{1}H-NMR spectra were collected for the series. Conversion was determined by measuring the reduction of the allyl proton resonance at 3.9 ppm relative to the methyl resonance at 3.0 ppm.

Formulation D (Dye 5/DCPD/TMCTS). The following procedure illustrates the procedure used to prepare prepolymers with added DCPD. A solution containing dye **5** (0.17 g, 1.0 mequiv of olefin), TMCTS (0.36 g, 6.0 mequiv of SiH), and toluene (0.88 g) was preheated in a sealed polytube to 65 °C. Diluted PCO72 catalyst (21 μL) was added, and the mixture was stirred for 3 h. The mixture was cooled in an ice bath, followed by addition of DCPD (0.33 g, 5.0 mequiv) and diluted PC072 catalyst (34 μL). The mixture was stirred at room temperature overnight.

Formulation E (Dye 7/TMCTS). The following procedure illustrates the procedure used to prepare prepolymers with no added DCPD. A solution containing dye **7** (0.752 g, 5 mequiv of olefin), TMCTS (0.302 g, 5 mequiv of SiH), and toluene (0.79 g) was heated in a sealed polytube for 10 min at 55 °C. Diluted PC072 catalyst (39 μL, 100 ppm Pt) was added, and the mixture stirred for 2 h at 55 °C. The mixture was stored in a refrigerator overnight.

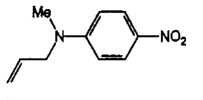
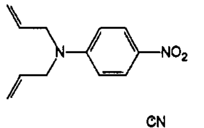
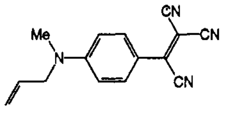
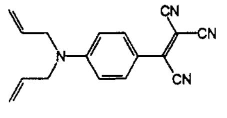
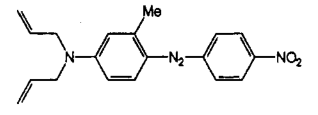
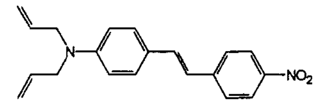
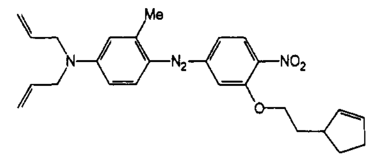
Corona-Poled Films, Formulation 5. The above prepolymer solution was diluted with toluene (1.15 g), and the solution was filtered to remove particulates. The solution was spin-cast onto soda lime substrates until dry. The films were precured at 130–190 °C and subjected to corona poling while gradually increasing the temperature of the film over several hours. The corona field was maintained while cooling the film to room temperature.

Results and Discussion

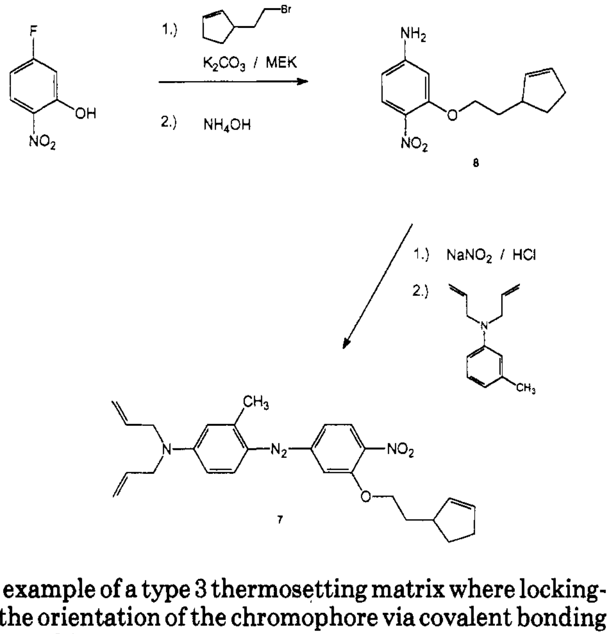
Synthesis. The dyes investigated in the hydrosilation reactions are listed in Table 1. Dye **1** was prepared by direct alkylation of *N*-methyl-4-nitroaniline with allyl bromide. Dye **2** was prepared from 4-fluoronitrobenzene by treatment of diallylamine using a procedure described for saturated analogs.[9] Dyes **3** and **4** were prepared by treatment of *N*-allyl-*N*-methylaniline and *N,N*-diallylaniline with tetracyanoethylene.[10] Dyes **5** and **6** were prepared by standard diazonium coupling reaction and stilbene condensation reactions, respectively.

Dye **7** is an azo chromophore containing three double bonds reactive toward hydrosilation, situated at two different sites on the chromophore π system. This provides

Table 1. Dyes Useful in Preparing Cross-Linked Organosilicon Polymers

Dye Number	Structure
1	
2	
3	
4	
5	
6	
7	

Scheme 2. Synthesis of Multisite Reactive Dye 7



an example of a type 3 thermosetting matrix where locking-in the orientation of the chromophore via covalent bonding is possible.

Dye **7** was prepared according to Scheme 2. 3-(2-Bromoethyl)cyclopentene was prepared from 2-cyclopentene-1-acetic acid using the same procedure described for a similar compound.[11] Alkylation of 2-nitro-5-fluorophenol with 3-(2-bromoethyl)cyclopentene followed by amination with ammonium hydroxide provided the 4-nitroaniline **8**. Diazotization of **8** and coupling with *N*,*N*-diallyl-*m*-toluidine gave the azo dye **7** as an oil.

Kinetics. A primary concern was whether the charge transfer molecules necessary for high NLO responses would be compatible with hydrosilation reactions. Initial experiments were designed to determine the reactivity of various olefinic chromophores toward hydrosilation by following the disappearance of allylic hydrogens on the chromophores with ^{1}H NMR.

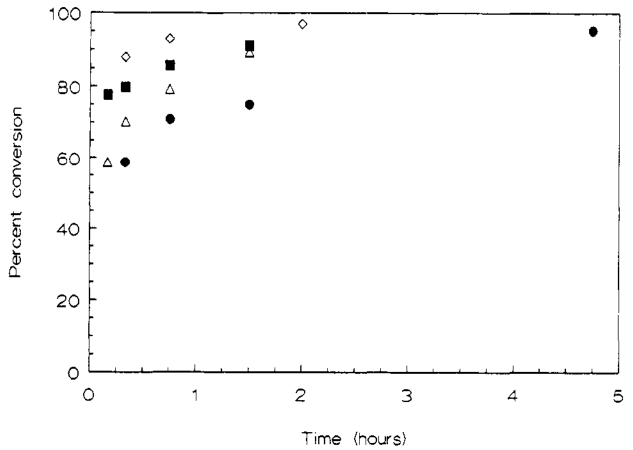


Figure 1. Hydrosilation kinetics: percent conversion of **1** (●), **2** (■), **5** (△), and **6** (◇) (2:1 ratio of SiH:olefin, toluene, PC072 catalyst, 65 °C) as determined by ^{1}H NMR.

The catalyst used in all hydrosilation reactions was PC072, a platinum divinyltetramethyldisiloxane complex in xylene (3.0–3.5% Pt). Catalyst concentration was usually about 100 ppm Pt relative to the total solids (TMCTS + dye + diolefin).

Figure 1 shows the rate of hydrosilation (65 °C, toluene, 2:1 ratio of SiH to olefin) of several allyl-containing chromophores with nitro electron-withdrawing groups. Comparison of the rate of hydrosilation of **1** with that of the diallylnitroaniline **2** shows that hydrosilation of the diallyl chromophore is somewhat faster, indicative of a catalysis activation by the diallyl moiety or, possibly, a proximity effect—the monohydrosilated adduct undergoing the second hydrosilation in an intramolecular fashion. Comparison of the rate of hydrosilation of diallyl chromophores **2**, **5**, and **6** at 65 °C with a 2:1 SiH:olefin ratio shows that stilbene **6** is most reactive toward hydrosilation, followed by the nitroaniline **2**, and the azo chromophore **5**. Each of these compounds is hydrosilated to 90% or better within 1.5 h. Thus, there appears to be little effect on the rate of hydrosilation with a change in the aromatic π system.

Hydrosilation of the 4-(tricyanovinyl)aniline **3** did not proceed at 65 °C. Subsequent addition of nitroaniline **1** to the reaction also showed no hydrosilation, indicating that the catalysis was no longer active. At 110 °C with a 2:1 ratio of SiH:olefin, **3** underwent hydrosilation, giving 80% conversion within 1 h (Figure 2). The conversion of both **3** and **4** appeared to level off at 80–85%, and there is no significant difference in reactivity under these conditions. A possible explanation may be that at 65 °C the binding constant for the tricyanovinyl group to the platinum catalyst is larger than the binding constants associated with catalyst activation by olefin. At temperatures high enough to release the tricyanovinyl group, the activation by the diallyl moiety over that of the monoallyl moiety is negligible. The difference in activity between **1** and **2** and between **3** and **4** at 65 and 110 °C, respectively, may be a consequence of different activation energies for the two distinct hydrosilation reactions that occur in the hydrosilation of diallyl groups.

Prepolymer and Film Formation. Cross-linkable prepolymers were prepared by hydrosilation of the desired chromophores with TMCTS in toluene. In cases where no DCPD was desired, the SiH:olefin ratio was 1:1 and the initial cure was terminated before the onset of gelation.

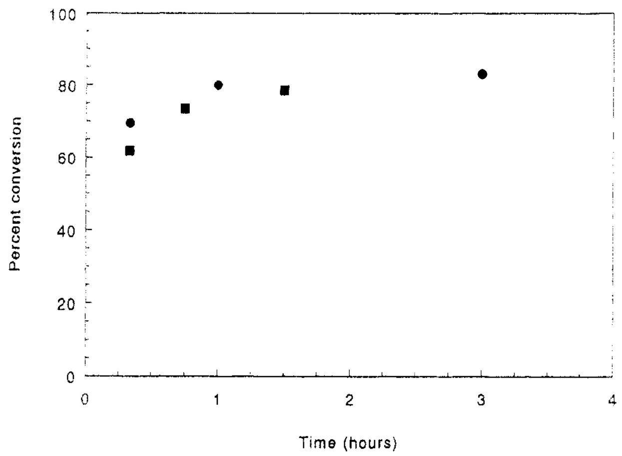


Figure 2. Hydrosilation kinetics: percent conversion of **3** (●) and **4** (■) (2:1 ratio of SiH:olefin, toluene, PC072 catalyst, 110 °C) as determined by ^{1}H NMR.

Table 2. Physical Parameters of Hydrosilation Systems

formulation[a]	N (mmol/cm^3)	λ_{max} (nm)	d_{31} (pm/V)	$T_{50\%}$ (°C)
A. 1.00:1.00 dye **2**:TMCTS	3.1	410	5 ± 2	129
B. 1.00:1.00 dye **4**:TMCTS	2.4	502	30 ± 9	103
C. 1.00:1.00 dye **5**:TMCTS	2.0	482	28 ± 8	123
D. 0.17:0.83:1 dye **5**:DCPD:TMCTS	0.3	482	5 ± 2	146
E. 1.00:1.00 dye **7**:TMCTS	1.6	470	3 ± 1	>190

[a] Ratio is milliequivalents of olefin versus milliequivalents of SiH.

Hydrosilation of dicyclopentadiene is known to proceed selectively at the 2,3 double bond at relatively low temperature.[12] At higher temperatures the cyclopentenyl double bond undergoes hydrosilation to provide cross-linked polymers.[13] Another approach to prepare cross-linkable prepolymers took advantage of this dual reactivity. Thus, in cases where DCPD was desired as a cross-linker, the chromophores were precured in the absence of DCPD, and the initial SiH:olefin ratio was greater than 1:1. DCPD was then added to bring the SiH:olefin ratio to 1:1, and a room temperature cure of DCPD was allowed to proceed.

Thin films of the prepolymers were spun onto soda lime glass substrates and subjected to a precure heat cycle at 130–190 °C. The thicknesses of the prepolymer thin films were measured using a Tencor Alpha-Step Profiler and generally ranged from 0.5 to 2 µm. For second-order NLO applications such as second-harmonic generators and electrooptic devices, the NLO moieties in the polymer must be aligned to make the polymer noncentrosymmetric. Corona poling was used to break symmetry in the films during the final cures at elevated temperature.[14] Various prepolymer formulations characterized as poled thin films are listed in Table 2.

SHG Measurements. Second-harmonic generation (SHG) experiments were utilized for the quick screening of hydrosilation materials. SHG measures the efficiency of a second-order nonlinear optical material to convert light at one wavelength (fundamental) to light at half the wavelength (second harmonic) as a function of fundamental polarization, second-harmonic polarization, and input angle of the fundamental light beam.

Theoretical fits to the experimental data (referred to as Maker fringes) gave the magnitude of the second-order nonlinearity of the hydrosilation materials.[15] Figure 3 demonstrates a typical Maker fringe spectrum for a thin-film hydrosilation polymer poled normal to the film plane. Since the thicknesses of the polymer thin films were less than the SHG coherence length, the Maker fringe spectra did not show oscillatory behavior for any of the hydrosilation formulations.

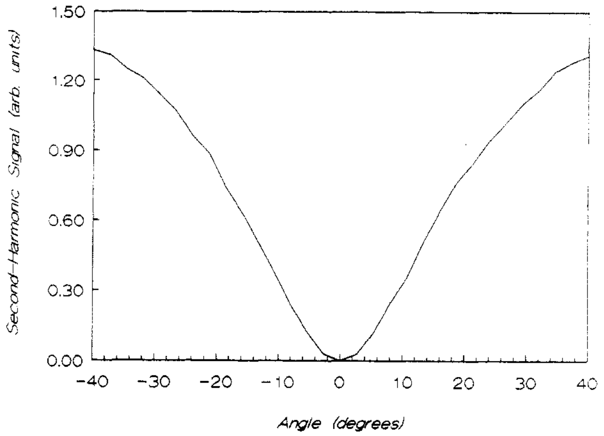


Figure 3. Maker fringe spectra of formulation C (1:1 dye **5**:TMCTS). Sample was poled normal to the film plane, and SHG experiment was configured for d_{31}.

For the work presented here, the SHG experimental system was configured for the unique determination of the d_{31} second-order coefficient. Since the second harmonic was slightly resonant in most of the systems studied, the d_{33} coefficient is not uniquely determined for polymers poled normal to the film plane (i.e., Kleinman symmetry may not be strictly applied). However, d_{33} is generally accepted to be at least 3 times the value for d_{31}.[16] The nonlinear properties were measured at a fundamental wavelength of 1.3 µm. The reference material was $LiNbO_3$ with an NLO coefficient, d_{33}, of ca. 30 pm/V. Absorption of the second-harmonic wavelength (absorption of the fundamental was negligible for all systems studied) was considered in the analysis of the Maker fringes.

Thermal stability of the second-order polymer is important for practical applications. The thermal characteristics of the second-order nonlinearity were measured by monitoring the SHG signal as a function of temperature. The sample was placed in the fundamental beam at a fixed orientation while the temperature of the sample was ramped from 30 to 190 °C in 8 °C steps. The sample was maintained at the new temperature for 1 min before the measurement was made.

The SHG thermal scan technique correlated well with the more traditional methods of determining thermal stability such as differential scanning calorimetry (DSC), dielectric relaxation, and long-term exposure to elevated temperatures.[17] In thermosetting epoxy NLO systems, we found that the temperature at which the SHG signal decayed to 50% of the maximum ($T_{50\%}$) was approximately the same as the glass transition as determined by DSC, and $T_{90\%}$ corresponded to the onset of dielectric relaxation.[17] Establishing similar correlations with the hydrosilation resins described here may be possible. However, because we were most interested in SHG stability of thin poled films, glass transitions and dielectric relaxations of bulk polymers were considered less relevant to this study than direct SHG monitoring with temperature.

SHG Measurements of Hydrosilation Formulations. Table 2 gives the corresponding linear and nonlinear physical parameters of the poled hydrosilation systems comprised of several chromophores listed in Table 1. The molar densities, N, for the hydrosilation systems were calculated assuming a density of 1 g/cm^3. λ_{max} is the peak

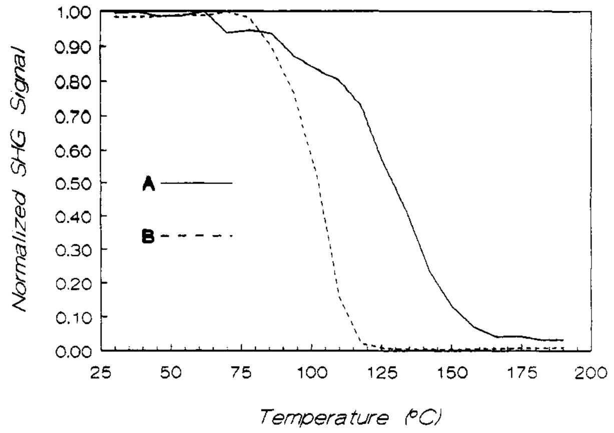


Figure 4. SHG thermal scans of formulations A and B. The angular position of the samples relative to the incident fundamental beam was fixed at 30°.

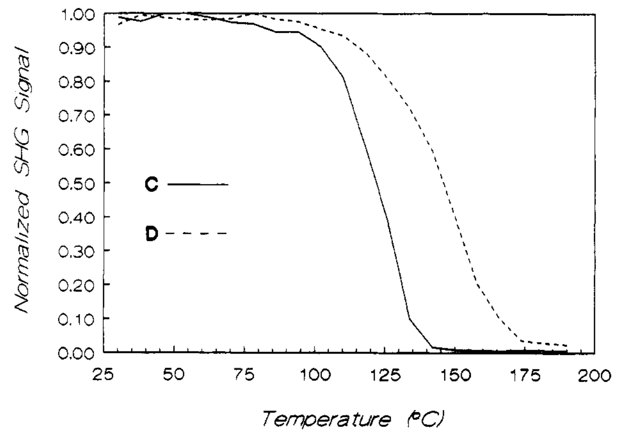


Figure 5. Effect of DCPD on the thermal properties of hydrosilation systems.

absorbance wavelength for the given polymer system, d_{31} is the second-order nonlinear coefficient determined from a numerical fit to the Maker fringe spectrum, and $T_{50\%}$ is as defined above.

Prepolymer formulations A–D examples of type 2 polymers that utilize side chain chromophores possessing hydrosilation reactive groups at one site on the chromophore. Side chain attachment of the chromophore allows for some mobility during poling which potentially leads to higher order and higher second-order nonlinearities. The matrix should cross-link around the chromophore, resulting in better thermal properties than a linear polymer.

Figure 4 depicts the SHG thermal stability data for formulations A and B. Dye **4** in formulation B was highly resonant with the second-harmonic, which resulted in a significantly higher value for the nonlinear coefficient despite the lower loading. Formulation A had superior thermal stability to that of formulation B and, also, had a residual nonlinearity of approximately 1 pm/V at 190 °C. The cause of the poor thermal stability of formulation B may be the partial inhibition of the hydrosilation cross-linking reaction by dye **4** as evidenced in the kinetic run showing only 85% conversion in the hydrosilation reaction at 110 °C over extended reaction times.

The effect of the cross-linker, DCPD, on the SHG thermal properties is demonstrated in Figure 5. Formulations C and D differ only by the presence of DCPD in formulation D. The larger π system in dye **5** improved the magnitude of the nonlinearity for formulations C and D over formulations A and B under similar loading conditions. It is clear from Figure 5 and Table 2 that the DCPD improved the SHG thermal properties. The residual nonlinearity at 190 °C was ca. 1 pm/V for formulation D.

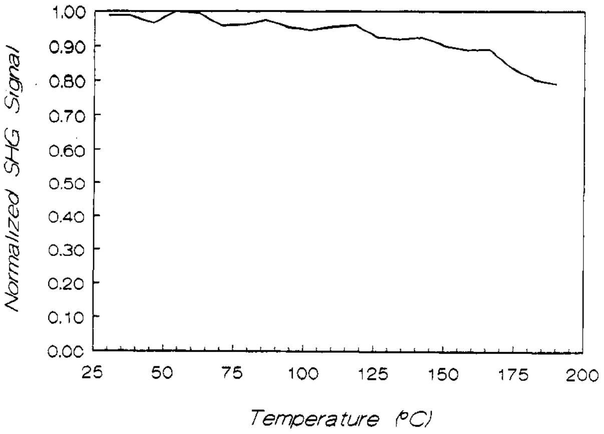


Figure 6. SHG thermal scan of formulation E.

Prepolymer formulation E is an example of a type 3 polymer that utilizes a chromophore possessing hydrosilation reactive groups at two different sites on the chromophore π system. Multisite reactivity may lock-in the orientation of the chromophore in the thermosetting matrix. In addition, the cyclopentene group of dye **7** has a lower reactivity toward hydrosilation than allyl groups, which may allow the chromophore to attain higher degrees of alignment before cross-linking.

Figure 6 plots the SHG thermal stability of formulation E comprised of dye **7** and TMCTS. While maintaining a nonlinearity of d_{31} = 3 pm/V, formulation E demonstrates thermal stability in excess of 190 °C. Limitations of the heating system prevented evaluation of the SHG signal above 190 °C. The SHG thermal stability exhibited by formulation E clearly exceeds the performance of the other formulations described here and in other thermosetting matrices described elsewhere.[3b,5b–i] This improvement in SHG thermal stability demonstrates the value of locking-in the chromophore orientation with multisite covalent bonding.

Summary

We have combined the excellent properties of the hydrosilation thermosetting matrix with chromophores that possess high second-order polarizabilities to produce novel thermosetting NLO materials. Formulations have been illustrated with high nonlinearities and reasonable thermal stability. In the one case where the NLO chromophore possessed the capability for multisite covalent bonding, which locked-in the orientation of the chromophore, the SHG thermal stability has clearly exceeded the current state of the art. Optimization of the chemistry, curing, and poling schedule should lead to systems that exhibit excellent nonlinear optical and thermal properties.

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