

# Fumaryl Chloride and Maleic Anhydride-Derived Crosslinked Functional Polymers for Nonlinear Optical Waveguide Applications

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**ABSTRACT:** The synthesis, processing, and characterization of new crosslinked functional polymer thin films derived from fumaryl chloride and maleic anhydride is presented. Experimental data demonstrated that this is a versatile, convenient, and cost-effective method of fabricating ultrastructure crosslinked and functional polymer thin films for potential nonlinear optical (NLO) or other applications where molecular orientation is required. The unsaturated and processable polyester thin films are capable of crosslinking in air to form a hardened lattice under a variety of conditions, including both thermal and photoinitiated crosslinking. The thermal stability of the second harmonic

(SHG) signal for a crosslinked NLO thin film was stable at temperatures up to 150°C, which is in contrast to uncrosslinked polymers whose SHG signals typically decreased over 50% below 100°C. Because of the lack of NH/OH groups and their vibrational overtones in the polymer, these crosslinked polyester systems have a great potential for low optical loss applications at 1550 nm communication wavelength. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 317–322, 2004

**Key words:** nonlinear optical (NLO); crosslinking; orientation; photopolymerization; solid-state polymerization

## INTRODUCTION

The advantages of using polymer thin films over conventional inorganic crystals in photonic devices include, but are not limited to: more versatile and convenient materials synthesis and device fabrication schemes, tunability of the materials electrical, optical, and other physical properties by molecular and supramolecular structure design and modifications, small dielectric constant, light weight, flexible shape, ultrafast signal response, less signal mismatch and lower coupling optical loss between the optic fibers and chips, and lower cost on large-scale manufacturing, for example.<sup>1–9</sup> In the case of an electro-optical (EO) modulator such as a Mark Zehnder interferometer, devices fabricated from NLO polymers have recently demonstrated the smallest half-wave switching voltage ( $V_{\pi}$ ) of 0.8 V<sup>3</sup> and a very large detectable bandwidth up to 1600 GHz,<sup>4</sup> and these values have far exceeded the best values achieved in inorganic NLO devices (i.e.,  $V_{\pi}$  of at least 5 V and bandwidth of less than 100 GHz).<sup>3–5</sup> However, for these successes, effec-

tive NLO polymer thin film ultrastructure fabrication with good molecular orientation stability and low optical loss are a few of the remaining challenges for realizing commercial polymeric electro-optical devices.<sup>5–7</sup>

For future optical communications systems operating at the 1550-nm wavelength, recent studies have revealed that vibrational overtones of organic hydroxyl (O—H) and amino (N—H) groups significantly contribute to the absorption-induced materials optical loss.<sup>6</sup> As a result, polymeric materials systems that do not contain O—H or N—H groups are more desirable. With respect to the materials' ultrastructure fabrication and thermal stability issue, crosslinked polymer systems are among the most promising systems because of their versatile processability, potentially very high thermal stability, and chemical resistance by polymer crosslinking.<sup>7–13</sup>

Maleic anhydride (MA)-derived unsaturated polyester resins have been studied for organic coatings and related commercial applications with either thermal or photoinitiated crosslinking protocols.<sup>14–16</sup> MA has also been used for synthesizing high  $T_g$  non-crosslinked NLO polymers.<sup>17</sup> Fumaryl chloride (FC) has been studied for polymer membrane applications.<sup>18</sup> We studied MA- and FC-derived crosslinked polyester resins for photonic thin film applications for several reasons. First, these crosslinked polyesters do not contain OH or NH groups, and are thus attractive

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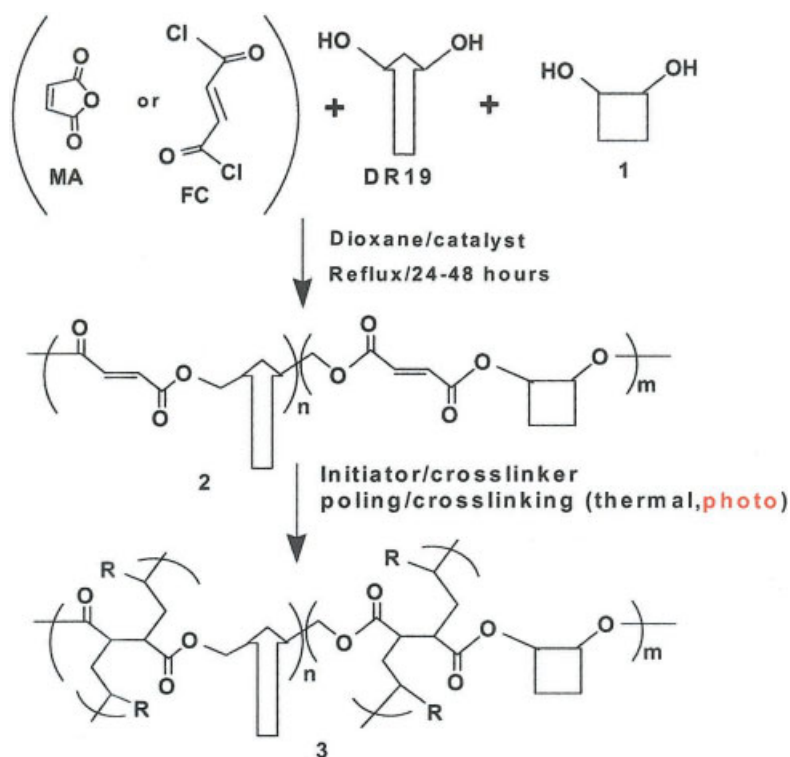


Figure 1 General synthetic and processing scheme of PDRFC/PDRMA.

for potential optical applications at 1550 nm. Second, the polymer synthesis and crosslinking schemes seem relatively versatile, convenient, and cost effective compared to most other developed crosslinked NLO polymer systems.<sup>7-13</sup> Finally, the capability of photoinitiated crosslinking of these polyesters<sup>16</sup> offer potential advantages of photolithographic protocols for waveguide ultrastructure fabrications.

## EXPERIMENTAL

A general synthetic and processing scheme is shown in Figure 1. In the first step, FC or MA condenses with an NLO chromophore diol, such as Disperse Red 19 (DR-19) in our case, and another nonchromophore diol (such as ethylene glycol) to form an unsaturated NLO polyester **2**. A nonchromophore diol comonomer **1** can be used to partially replace DR-19 to fine-tune the NLO chromophore loading and other physical properties of the NLO polymers. It can also minimize the electrostatic interactions between the NLO chromophore that generally negatively affect chromophore orientations, particularly for high  $\mu\beta$  chromophore systems.<sup>19-21</sup>

In the case of fumaryl chloride synthesis, for example, 1.9 mmol of DR-19 was dissolved in 25 mL of dry dioxane under nitrogen gas in a three-neck flask, then 4.7 mmol of ethylene glycol (diol) was added to the

flask (so that a 30% loading percentage of DR-19 in the polymer can be achieved). The mixture was preheated to 40°C, to which 6.6 mmol of FC was diluted in 10 mL of dry dioxane and added dropwise to the mixture over a period of 30 min. Unlike MA, which is relatively slow to react, FC reacts very quickly with the mixture at this lower temperature. Adding 2.5 mL of pyridine per 1 g of FC is required to completely remove the reaction-generated HCl byproduct, and it also greatly facilitates the polymer formation. The resulting suspension was stirred for 24–48 h. A dark red viscous and gummy precipitate was collected by extraction and washed with hexanes and water to yield a solid dark red product of PDRFC (polymer of DR-19 and fumaryl chloride) with typical yield of 70%. The acidity of extracted solvent was tested by litmus paper to ensure neutralization of acid.

In the case of synthesis using MA, a few drops of mineral acids such as HCl coupled with a Dean–Stark trap was used to facilitate the formation of polyesters. The resulting dark red solution was concentrated in a rotary evaporator and excess solvent was removed. A dark red solid product was precipitated from the concentrated solution when cold methanol was added. A red precipitate was purified using silica gel column eluted with a mixture solvent (80% ethyl acetate versus 20% hexane). The purified product was reprecipitated from 60% aqueous methanol, at a typical yield of 38%. The progress of the polymerization reaction

was continuously monitored with TLC for both schemes. The formation of the polymer can be detected by observing the development of a dark spot on the TLC. To remove any remaining low molecular weight polymer, samples can be redissolved and reprecipitated.

### NMR spectroscopy

$^1\text{H}$ -NMR spectra were recorded at a Bruker Avance 300 MHz spectrometer (Bruker Instruments, Billerica, MA) with TMS as internal reference. For monomer  $^1\text{H}$ -NMR spectra, 64 scans were usually taken. For polymers, 1500 scans were typically needed to achieve a good signal-to-noise ratio. The proton-decoupled  $^{13}\text{C}$ -NMR spectra were recorded on the same instrument with 25,000–40,000 scans to achieve an acceptable signal-to-noise ratio.

### FTIR spectroscopy

The FTIR spectra ( $4000\text{--}550\text{ cm}^{-1}$ ) were obtained on a Nicolet Avator FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). A series of eight scans were collected for each sample. Homogeneous polymer thin films were formed on the NaCl IR cell from drops of a diluted solution of linear polymer or an aliquot of polymer sample applied on the cell directly and followed by evaporation of solvent. Solid IR samples were made using KBr pellets.

### Molecular weight measurement

Polymer molecular weights were measured employing a Viscotek Tri-Sec T60/LR40 GPC (gel permeation chromatography) system (Viscotek, Houston, TX) with mobile phase of THF in ambient temperature. Polystyrenes were used as reference standards.

### Thermal analysis

Perkin–Elmer DSC-6 (differential scanning calorimeter) and TGA-6 (thermal gravimetric analysis) systems (Perkin Elmer Cetus Instruments, Norwalk, CT) were employed to characterize the thermal stability of the polymer samples. The heating rate of  $10^\circ\text{C}/\text{min}$  was used to obtain higher sensitivity and collect more data in each scan.

### UV–vis spectroscopy

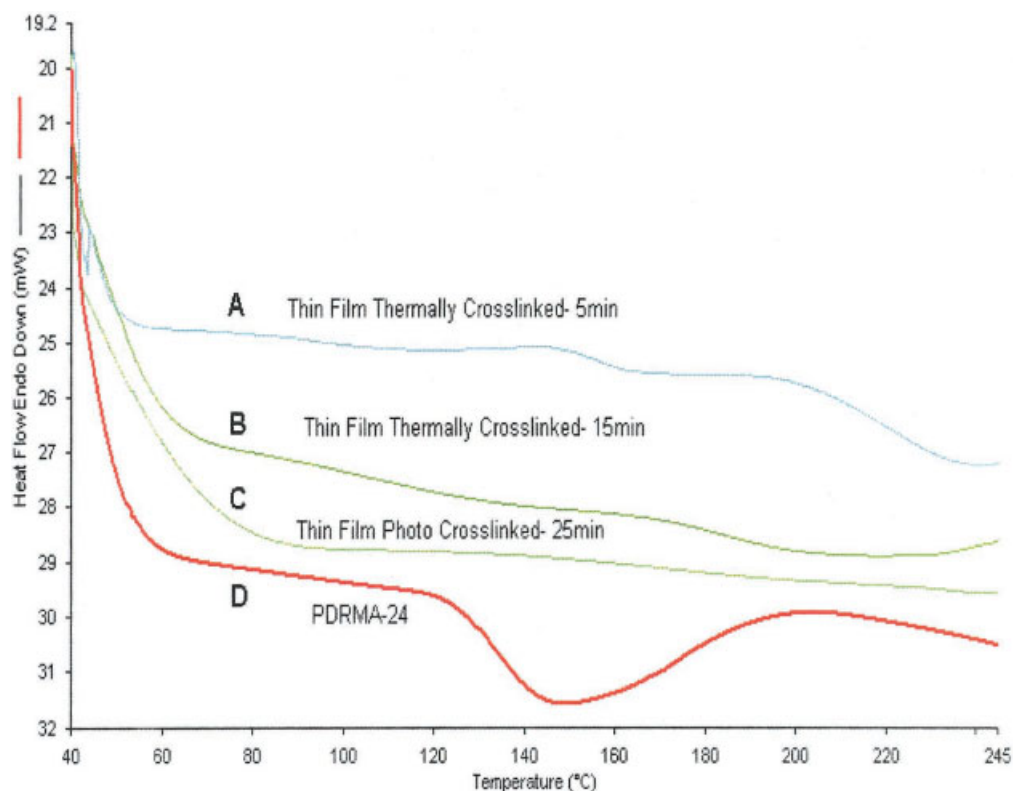
A Varian Cary 5G UV-Vis-NIR double-beam spectrophotometer (Varian Associates, Palo Alto, CA) was used to measure the absorbance of polymer film samples between 250 and 850 nm at room temperature. A bare ITO substrate was used as a reference.

## RESULTS AND DISCUSSION

Both FC and MA coupled with DR-19 yielding unsaturated NLO polyesters **2** and final crosslinked NLO polyesters **3** with almost the same chemical, physical, and optical properties. All synthesized polyesters were characterized by NMR, elemental analysis, IR, DSC, TGA, GPC, and UV–vis. For instance, the  $^1\text{H}$ -NMR of synthesized polyesters **2** showed that the two hydroxyl protons of DR-19 at 4.9 ppm disappeared, whereas that of the MA or FC alkene protons at 6.2–6.4 ppm still remained. Also, the methylene proton peaks of DR-19 became much broadened after polymer formation. Elemental analysis results of a typical polymer sample **2** ( $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_6$ )<sub>n</sub>: calcd: C, 58.54%; N, 13.65%; H, 4.42%. Found: C, 58.61%; N, 13.69%; H, 4.38%. GPC (calibrated with polystyrene standards, THF as solvent) analysis showed the synthesized unsaturated polyesters' molecular weight (MW) varies between  $8 \times 10^3$  to  $5 \times 10^4$  (g/mol) for 24–48 h polymer reaction time. Thermal analysis shows the synthesized unsaturated polyesters exhibited a typical glass-transition temperature between 120 and  $140^\circ\text{C}$ , and that the decomposition temperatures (in air) varied between 300 and  $350^\circ\text{C}$  depending significantly on the chromophore loading and the molecular weight. Thermal gravimetric analysis (TGA) showed the thermal decomposition temperature ( $T_d$ ) of the synthesized NLO polyester **2** is better compared to that of DR-19 chromophore. This is sometimes the case because the polymer matrix helps to slow down the materials' oxidative degradation.<sup>19</sup>

The IR data of pure DR-19 chromophore has a broad peak at  $3386\text{ cm}^{-1}$  attributed to the presence of hydroxyl (OH) groups. That this broad hydroxyl peak disappeared in synthesized polyesters also demonstrated the formation of polymer. The disappearance of OH groups and their vibrational overtones between 1400 and 1600 nm are very critical for low optical loss applications at 1550 nm.<sup>6</sup> Two major peaks are observed for polymers at around 1735 and  $1654\text{ cm}^{-1}$  attributed to ester groups and alkene bonds, respectively. A new small shoulder peak appears at  $989\text{ cm}^{-1}$ , indicating more *trans* than *cis* C—H stretching in the alkene bonds.<sup>22</sup> This evidence and previous MA-derived polymer studies suggest that the synthesized unsaturated polyesters are in predominantly *trans* (fumarate) configuration.<sup>23</sup>

All crosslinking reactions of polymer thin films were carried out in air. To fabricate thin films, the unsaturated polyester solids were first dissolved in cyclopentanone or DMF. An equivalent molar amount of vinyl crosslinkers, such as styrene, methylmethacrylate (MMA), triethylene glycol divinyl ether (TEG), 1,4 cyclohexane dimethanol divinyl ether (CDE), or bis[4-(vinylloxy)butyl] succinate (VBS) were added. A



**Figure 2** DSC studies of crosslinking reactions of 2: (A) thermal crosslinking for 5 min; (B) thermal crosslinking for 15 min; (C) photocrosslinking for 25 min; (D) without crosslinking.

crosslinking initiator (1–3 wt %) was also dissolved together in polymer solution.

For thermally induced crosslinking, a common vinyl crosslinker such as a styrene or MMA coupled with a common radical initiator such as benzoyl peroxide worked well. For photoinduced crosslinking, a photosensitizing initiator such as tetrabromofluoroscine, and a donor type of crosslinkers such as TEG, CDE, or VBS were used. After dissolution, polymer solutions were filtered through a 0.2- $\mu\text{m}$  filter, then spin coated on ITO glass slides with a thickness between 2 and 50  $\mu\text{m}$  depending on the purpose of the thin film study. We also used a second set of samples without any initiator for comparison study. The films were then dried in a vacuum oven at 50°C for at least 24 h.

For thermal crosslinking, the dried films were heated to near the glass-transition temperature  $T_g$  (typically 120–130°C), and electric field poled with a 5- to 9-kV dc electric field on a corona poling stage. Both IR and DSC indicated the crosslinking reaction typically completed within 20–30 min. The crosslinked polymer films were then cooled to room temperature in the presence of the poling electric field. As shown in Figure 2, the uncrosslinked polymer  $T_g$  (curve D) either shifted toward much higher temperatures with partial crosslinking (curve A), or disappeared with sufficient crosslinking (curve B). FTIR spectra indi-

cated the reduction or complete disappearance of the polymer alkene bond  $\text{C}=\text{C}$  stretching around 1650  $\text{cm}^{-1}$  after crosslinking. The crosslinking reaction can also be conveniently characterized by solubility test. The polyester thin films were soft and soluble in polar solvents such as acetone before crosslinking, and the film became rigid and insoluble after crosslinking.

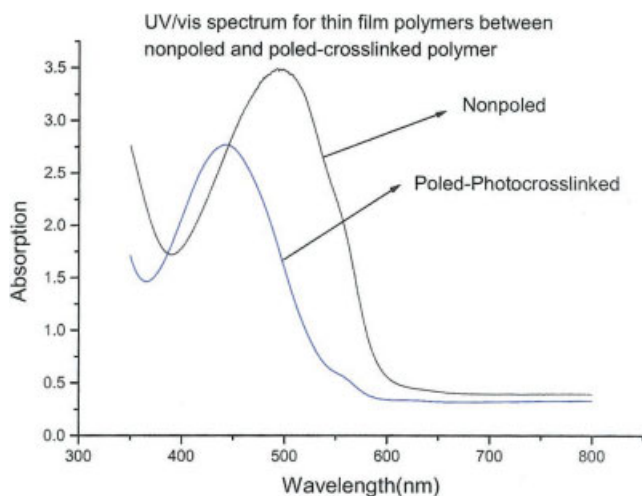
For visible light photocrosslinking, a visible light source (Oriel 1 kW QTH lamp; Oriel, Stratford, CT) was used. Because of the lack of thermal initiator benzoyl peroxide, the unsaturated polyesters doped with photoinitiator tetrabromofluoroscine were found thermally crosslinked only above 160°C, well over the  $T_g$  of these polyesters. In the photocrosslinking experiment, the polyester films were heated near the  $T_g$  (~120°C), corona poled, and irradiated with a collimated beam (3-in. diameter) of visible light of 150  $\text{mW}/\text{cm}^2$  radiant power on film surface. Curve C in Figure 2 shows the DSC scan of a photocrosslinked polymer thin film.

Before crosslinking, the polymer thin films were soft and soluble in polar solvents such as acetone and DMF. After crosslinking, a rigid and insoluble film was formed. The crosslinked polymer films were immersed in DMF for 2 h and less than 5% weight loss was observed for these films. The solvents did not extract any measurable concentration of the polymer as examined by FTIR and UV-vis spectroscopy. These

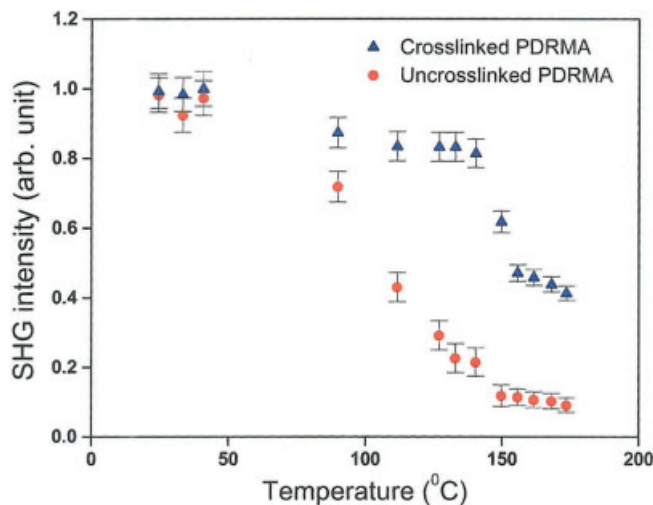
results indicated that the NLO chromophores were firmly locked into the three-dimensional network formed by crosslinking of polyester backbones. In comparison, those thin films without initiator showed no crosslinking under the same conditions. We speculate that simply heating the samples to their glass-transition temperature ( $T_g$ ) under the same conditions will not generate enough free radicals to cause significant crosslinking.

Figure 3 shows a typical UV-vis absorption spectrum of the polymer **2** before and after corona poling and crosslinking. In the figure, the DR-19 charge transfer peak at about 510 nm shifts to a shorter wavelength upon poling. The intensity of the absorbance also drops because of chromophore orientation change from random to aligned perpendicular to the plane of the film. This reduction in the absorption intensity and the blue shift to higher energy are both consistent with electrochromic shifts in poled polymer films previously observed.<sup>8-13</sup>

Second harmonic generation (SHG) measurements were performed on the films after corona poling. The setup used a Coherent Infinity Nd : YAG laser outputting 30 mJ/pulse with a 10-Hz repetition rate and 3-ns pulse width at 1064 nm. The beam was collimated into a 1-mm beam diameter. The second harmonic light in the beam path was collected, and spectrally filtered with interference filters and a 0.25- $\mu\text{m}$  monochromator before entering a P128 photomultiplier that has no sensitivity in the fundamental (1064 nm) laser wavelength. The signal was averaged in a digital oscilloscope, and the scattered light from a bare substrate was subtracted to measure the second harmonic intensity of the film. The substrate was rotated in the plane perpendicular to the path of propagation and the polarization of the incoming light to observe the angular dependency of the optical signal. Figure 4 shows the



**Figure 3** UV-vis spectra of polymer thin films **3** with or without poling.



**Figure 4** Normalized SHG signals versus polymer film temperature.

normalized SHG signals versus the heating temperature of the film. As the data demonstrated, the intensity of the SHG signal from an uncrosslinked polyester thin film started to decrease dramatically below 50°C, whereas for a crosslinked film, the SHG signal intensity was stable up to 150°C. However, with further optimization of the comonomers, crosslinkers, and crosslinking reactions, better SHG stability may be obtained. The optical loss measurement is in collaboration with other groups, and will be reported separately.

## CONCLUSIONS

In conclusion, a versatile and convenient protocol of synthesizing and fabricating ultrastructured and crosslinked functional polymer thin films was developed for fabricating nonlinear optical waveguides. Advantages of this system include adaptable, convenient, and cost-effective preparation of these materials. The synthetic scheme can be extended to incorporate a wide range of NLO (diol) chromophores with widely ranging loading capacity. Optical-quality thin films can be easily obtained. Low absorption optical loss at 1550 nm may be achieved because of the lack of OH/NH vibrational overtones, and excellent thermal stability with high density crosslinking. This protocol is also amenable for cost-effective photolithographic fabrication of photonic waveguide devices under visible light radiation.

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