

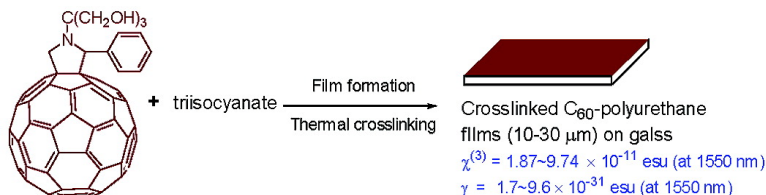
Communication

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## [60]Fullerene-Containing Polyurethane Films with Large Ultrafast Nonresonant Third-Order Nonlinearity at Telecommunication Wavelengths

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The third-order nonlinear optical (NLO) response is important in all-optical switching, signal processing, and ultrafast optical communications.<sup>1</sup> To be practically useful for all-optical switching, materials should have a large nonlinear refractive index ( $n_2$ ) at the operating wavelength, typically at 1.3–1.6  $\mu\text{m}$ , ultrafast response and relaxation times (picoseconds or less), minimal absorption loss (nonresonant nonlinearity), good environmental stability, and processability.<sup>2</sup>  $\pi$ -Conjugated organic compounds and polymers have been investigated as a new class of third-order NLO materials.<sup>3</sup> However, few organic materials reported to date offer a combination of the large nonresonant nonlinearity in the near-infrared (NIR) region, response time in picoseconds, and good film-forming properties. Polyacetylene, poly(phenylene vinylene), and their derivatives are typically lacking a desired processability and long-term photostability.<sup>3d</sup>

A large number of highly delocalized  $\pi$ -electrons of the fullerenes are a known contributor to fast response time and large optical nonlinearity of [60]fullerene ( $\text{C}_{60}$ ).<sup>4</sup> Furthermore, when double bonds are broken and an electron donor group is attached,  $\text{C}_{60}$  derivatives show prominent enhancement in molecular second hyperpolarizability  $\gamma$ , as compared with pristine  $\text{C}_{60}$ .<sup>5</sup> To realize the large third-order NLO susceptibility ( $\chi^{(3)}$ ) of  $\text{C}_{60}$  derivatives in a device, it is necessary to have a relatively thick, homogeneous film containing a high loading of  $\text{C}_{60}$  derivative and to preserve the high  $\gamma$  per  $\text{C}_{60}$  molecule even once it is being processed into a film ready for subsequent device fabrication.

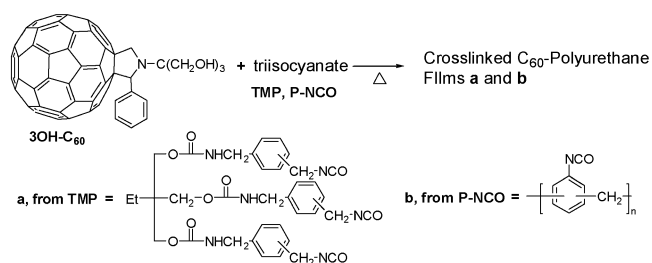
We report herein the largest third-order optical nonlinearity within a range of 1150–1600 nm of cross-linked polyurethane (PU) films containing a high content of covalently bonded  $\text{C}_{60}$ . The reported method is advantageously simple for preparation of high-quality  $\text{C}_{60}$  polymer films and also practically adaptable for making other NLO polymeric films.

$\text{C}_{60}$  was first functionalized using the well-established 1,3-dipolar cycloaddition of azomethine which is derived from an  $\alpha$ -amino acid and an aldehyde.<sup>6</sup> A trihydroxyl-containing  $\text{C}_{60}$  ( $3\text{OH-C}_{60}$ ) was prepared in good yield from  $\text{C}_{60}$ , tricine, and benzaldehyde and was purified by chromatography. The cyclic amine moiety in  $3\text{OH-C}_{60}$  is expected to contribute to the required charge transfer, and the hydroxyl groups are used for cross-linking with an isocyanate. In comparison with  $\text{C}_{60}$ ,  $3\text{OH-C}_{60}$  is more soluble in common organic solvents, such as tetrahydrofuran (THF), toluene, and  $N,N$ -dimethylformamide.

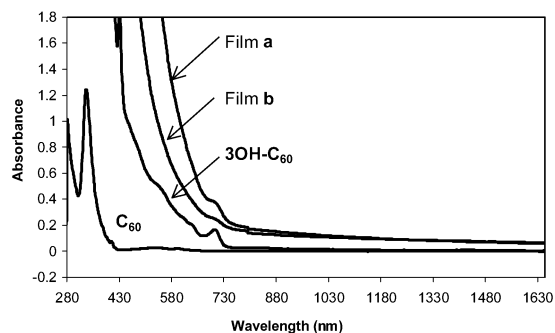
Two commercially available triisocyanates, **TMP** and **P-NCO**, were used in the prepolymer formulation with  $3\text{OH-C}_{60}$  (Scheme 1). Both films **a** and **b** contain 25 wt % of  $3\text{OH-C}_{60}$  (or 19.1 wt % of  $\text{C}_{60}$ ). Several processing factors are important to obtain high-quality films for  $\chi^{(3)}$  measurement (see experimental details in the

Supporting Information). Casting the film should be done in dry air, on a precleaned glass substrate at 50  $^{\circ}\text{C}$ . After drying at 50  $^{\circ}\text{C}$  overnight, the films were cured at 120  $^{\circ}\text{C}$  for 1 h, at 160  $^{\circ}\text{C}$  for another hour, and finally at 210  $^{\circ}\text{C}$  for 30 min.

### Scheme 1. Preparation of Cross-Linked $\text{C}_{60}$ -PU Films



IR spectra of polymer films **a** and **b** displayed a characteristic band at 527  $\text{cm}^{-1}$  due to the functionalized  $\text{C}_{60}$  cage in the polymer (see IR spectra in the Supporting Information). The carbonyl peak attributed to the urethane linkage as a result of covalent bonding between  $3\text{OH-C}_{60}$  and the triisocyanate was clearly seen at 1667  $\text{cm}^{-1}$  for film **b** but overlapped with the other amide peaks already presented in **TMP** for film **a**. Figure 1 shows a typical absorption of the  $\text{C}_{60}$  moiety around 330 nm for films **a** and **b**,  $3\text{OH-C}_{60}$ , and pristine  $\text{C}_{60}$ , which is known to become broad with a tail close to 700 nm for the substituted  $\text{C}_{60}$ .<sup>7</sup> There is no observable peak at 1000–2000 nm, allowing for measurement of the nonresonant nonlinearity at telecommunication wavelengths in this work. Thermogravimetric analysis indicated a good thermal stability for these films, with the onset temperature of 310  $^{\circ}\text{C}$  for 5% weight loss in nitrogen.



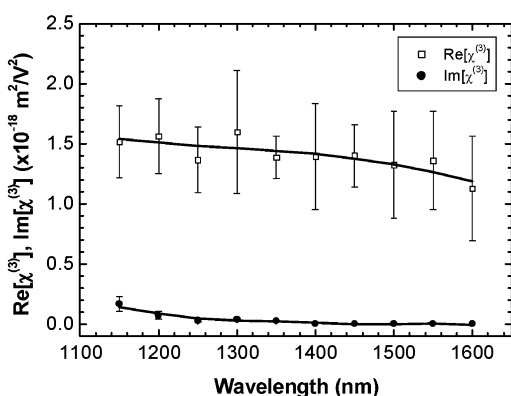
**Figure 1.** Absorption spectra of  $\text{C}_{60}$ -PU film **a** (30  $\mu\text{m}$ ), film **b** (10  $\mu\text{m}$ ),  $3\text{OH-C}_{60}$  in THF ( $5.3 \times 10^{-4}$  M), and  $\text{C}_{60}$  in toluene ( $1.0 \times 10^{-5}$  M).

The nonlinear refractive index or Kerr coefficient ( $n_2$ ) and nonlinear absorption coefficient ( $\beta$ ) for the  $\text{C}_{60}$ -PU films were measured by using the Z-scan technique with a laser pulse of 3.3 ps operating in the wavelength range of 1150–1600 nm at a

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wavelength interval of 50 nm. The Z-scan setup and data interpretation can be found elsewhere.<sup>8</sup> At 1550 nm, no valley or peak in the open-aperture curve is observed for film **a**, indicating that no nonlinear absorption exists (or  $\beta = 0$ ). Its Kerr coefficient  $n_2$  is measured to be positive,  $(2.0 \pm 0.6) \times 10^{-3} \text{ cm}^2/\text{GW}$ . For polymer film **b**, the  $n_2$  value is  $(3.7 \pm 0.8) \times 10^{-4} \text{ cm}^2/\text{GW}$  and the  $\beta$  value is essentially zero by similar measurement and theoretical fittings. Considering the two figures of merit for potential device applications,  $W = n_2 I / \alpha_0 \lambda$  and  $T = \beta \lambda / n_2$ , where  $I$  is the intensity of the incident light,  $\alpha_0$  is one-photon absorption, and  $\lambda$  is the wavelength of the light, it is necessary to achieve  $W \gg 1$  and  $T \ll 1$  for any materials to be practically useful for all-optical switching. Because the C<sub>60</sub>-PU films exhibit negligible one-photon absorption ( $\alpha_0$ ) throughout the region of 1150–1600 nm, the  $W$  value should be ideal, that is,  $W \gg 1$ . The  $T$  value near 1150 nm is marginal due to a nonlinear absorption at the wavelengths near 1150 nm, but satisfactory near 1550 nm. Therefore, C<sub>60</sub>-PU materials are deemed to be suitable for device applications at the NIR wavelengths.



**Figure 2.** Spectra of real part  $\text{Re}[\chi^{(3)}]$  and imaginary part  $\text{Im}[\chi^{(3)}]$  of the third-order NLO susceptibility of film **a**.

The  $\chi^{(3)}$  of polymer films constitutes two parts: the real part ( $\text{Re}[\chi^{(3)}]$ ) and imaginary part ( $\text{Im}[\chi^{(3)}]$ ) that are related to  $n_2$  and  $\beta$ , respectively. The spectra of ( $\text{Re}[\chi^{(3)}]$ ) and ( $\text{Im}[\chi^{(3)}]$ ) of film **a** derived from the experimental results are shown in Figure 2. The  $\chi^{(3)}$  value of film **a**, mostly contributed from  $\text{Re}[\chi^{(3)}]$ , falls in the range of  $(1.13\text{--}1.54) \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$  and at 1550 nm is  $1.36 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$  ( $9.74 \times 10^{-11} \text{ esu}$ ). Film **b** has a  $\chi^{(3)}$  value of  $2.61 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$  ( $1.87 \times 10^{-11} \text{ esu}$ ) at 1550 nm. The  $\gamma$  values for the C<sub>60</sub> moiety in films **a** and **b** are determined to be  $9.6 \times 10^{-32}$  and  $1.7 \times 10^{-32} \text{ esu}$  at 1550 nm, respectively. In comparison with other C<sub>60</sub> materials (Table 1), C<sub>60</sub>-PU films display the largest  $\chi^{(3)}$  value, typically in 1–2 orders of enhancement over recently reported C<sub>60</sub> materials. The  $\gamma$  values are also larger than other C<sub>60</sub> derivatives and polymers.<sup>3</sup> The observed large  $\chi^{(3)}$  values are clearly not attributed to the one-photon absorption, as there is no observable NIR peak (Figure 1). Furthermore, the two-photon absorption (TPA) does not appear to be responsible either, given the smoothness of the  $\text{Re}[\chi^{(3)}]$  curve over the full bandwidth extending from the possible TPA region into the clearly non-TPA region (beyond 1500 nm, Figure 1). The mechanism for this significant enhancement in our case is believed to be mainly due to the successful incorporation and well dispersion of large amount (19.1 wt % or the number density of  $1.9 \times 10^{20} \text{ cm}^{-3}$ ) of C<sub>60</sub> into a highly cross-linked polymer. A strong charge-transfer process in which C<sub>60</sub> acts as an electron acceptor and the substitute group serves as an electron donor also contributes to the enhancement of the optical nonlinearity. The difference in the  $\gamma$  values of the two films is about 5.6

times, which could be due to the presence of different dipolar domains or local field effects in the films caused by structurally different **TMP** and **P-NCO**.

**Table 1.** Comparison of Third-Order Optical Nonlinearity of C<sub>60</sub>-PU Films with Other C<sub>60</sub> Materials<sup>a</sup>

materials [ND]	$\chi^{(3)}$ , esu (wavelength)	$\gamma$ , esu
C <sub>60</sub> solution <sup>5a,b</sup> [(4.2–16.2) × 10 <sup>18</sup> ]	$5.8 \times 10^{-15}$ (452 nm)	$3.7 \times 10^{-35}$
C <sub>60</sub> <sup>-</sup> solution <sup>5a,b</sup> [(0.8–2.7) × 10 <sup>18</sup> ]	N/A (452)	$2.4 \times 10^{-33}$
C <sub>60</sub> (NH <sub>2</sub> CN) <sub>5</sub> solution <sup>5c</sup> [1.8 × 10 <sup>18</sup> ]	$5.8 \times 10^{-14}$ (830 nm)	$1.0 \times 10^{-32}$
C <sub>60</sub> -silane sol–gel <sup>5d</sup> [9.6 × 10 <sup>17</sup> ]	$1.4 \times 10^{-13}$ (820 nm)	not available
C <sub>60</sub> -PSt solution <sup>5f</sup> [3.9 × 10 <sup>18</sup> ]	$1.1 \times 10^{-12}$ (800 nm)	$6.6 \times 10^{-32}$
C <sub>60</sub> film <sup>5h</sup> [1.3 × 10 <sup>21</sup> ]	$9.6 \times 10^{-12}$ (1830 nm)	$4.3 \times 10^{-34}$
C <sub>60</sub> -PU film <b>a</b> [1.9 × 10 <sup>20</sup> (this work)]	$9.7 \times 10^{-11}$ (1550 nm)	$9.6 \times 10^{-32}$

<sup>a</sup> ND = number density of C<sub>60</sub> moiety ( $\text{cm}^{-3}$ ). PSt = polystyrene.

In conclusion, very large, ultrafast nonresonant third-order nonlinearity in the NIR region and specifically at 1550 nm was demonstrated with cross-linked C<sub>60</sub>-PU films. The availability of a wide range of functionalized C<sub>60</sub> and C<sub>60</sub>/polymer formulations opens a viable route to further development of suitable materials for all-optical switching devices.

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**Supporting Information Available:** Experimental details, IR spectra, and picture of free-standing film **a** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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