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

Li Kuang,[†] Qiying Chen,[‡] Edward H. Sargent,[‡] and Zhi Yuan Wang*,[†]

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6, and Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario, Canada M5S 3G4

Received July 30, 2003; E-mail: wangw@ccs.carleton.ca

The third-order nonlinear optical (NLO) response is important in all-optical switching, signal processing, and ultrafast optical communications.[1] To be practically useful for all-optical switching, materials should have a large nonlinear refractive index (n_2) at the operating wavelength, typically at $1.3-1.6$ μm, ultrafast response and relaxation times (picoseconds or less), minimal absorption loss (nonresonant nonlinearity), good environmental stability, and processability.[2] π-Conjugated organic compounds and polymers have been investigated as a new class of third-order NLO materials.[3] 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.[3d]

A large number of highly delocalized π-electrons of the fullerenes are a known contributor to fast response time and large optical nonlinearity of [60]fullerene (C_{60}).[4] Furthermore, when double bonds are broken and an electron donor group is attached, C_{60} derivatives show prominent enhancement in molecular second hyperpolarizability γ, as compared with pristine C_{60}.[5] To realize the large third-order NLO susceptibility ($\chi^{(3)}$) of C_{60} derivatives in a device, it is necessary to have a relatively thick, homogeneous film containing a high loading of C_{60} derivative and to preserve the high γ per 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 C_{60}. The reported method is advantageously simple for preparation of high-quality C_{60} polymer films and also practically adaptable for making other NLO polymeric films.

C_{60} was first functionalized using the well-established 1,3-dipolar cycloaddition of azomethine which is derived from an α-amino acid and an aldehyde.[6] A trihydroxyl-containing C_{60} ($\textbf{3OH-C}_{60}$) was prepared in good yield from C_{60}, tricine, and benzaldehyde and was purified by chromatography. The cyclic amine moiety in $\textbf{3OH-C}_{60}$ is expected to contribute to the required charge transfer, and the hydroxyl groups are used for cross-linking with an isocyanate. In comparison with C_{60}, $\textbf{3OH-C}_{60}$ 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 $\textbf{3OH-C}_{60}$ (Scheme 1). Both films **a** and **b** contain 25 wt % of $\textbf{3OH-C}_{60}$ (or 19.1 wt % of 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 °C. After drying at 50 °C overnight, the films were cured at 120 °C for 1 h, at 160 °C for another hour, and finally at 210 °C for 30 min.

Scheme 1. Preparation of Cross-Linked C_{60}-PU Films
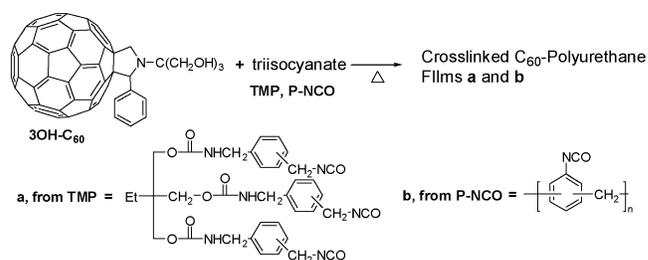
IR spectra of polymer films **a** and **b** displayed a characteristic band at 527 cm^{-1} due to the functionalized C_{60} cage in the polymer (see IR spectra in the Supporting Information). The carbonyl peak attributed to the urethane linkage as a result of covalent bonding between $\textbf{3OH-C}_{60}$ and the triisocyanate was clearly seen at 1667 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 C_{60} moiety around 330 nm for films **a** and **b**, $\textbf{3OH-C}_{60}$, and pristine C_{60}, which is known to become broad with a tail close to 700 nm for the substituted C_{60}.[7] 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 °C for 5% weight loss in nitrogen.
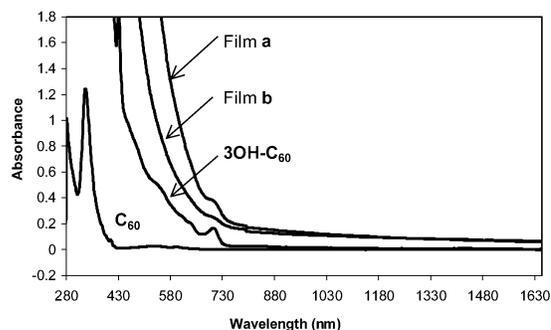

Figure 1. Absorption spectra of C_{60}-PU film **a** (30 μm), film **b** (10 μm), $\textbf{3OH-C}_{60}$ in THF (5.3×10^{-4} M), and C_{60} in toluene (1.0×10^{-5} M).

The nonlinear refractive index or Kerr coefficient (n_2) and nonlinear absorption coefficient (β) for the 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

† Carleton University.
‡ University of Toronto.

wavelength interval of 50 nm. The Z-scan setup and data interpretation can be found elsewhere.[8] 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, $(2.0 \pm 0.6) \times 10^{-3}$ cm^2/GW. For polymer film **b**, the n_2 value is $(3.7 \pm 0.8) \times 10^{-4}$ cm^2/GW and the β 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, α_0 is one-photon absorption, and λ 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$_{60}$-PU films exhibit negligible one-photon absorption (α_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$_{60}$-PU materials are deemed to be suitable for device applications at the NIR wavelengths.
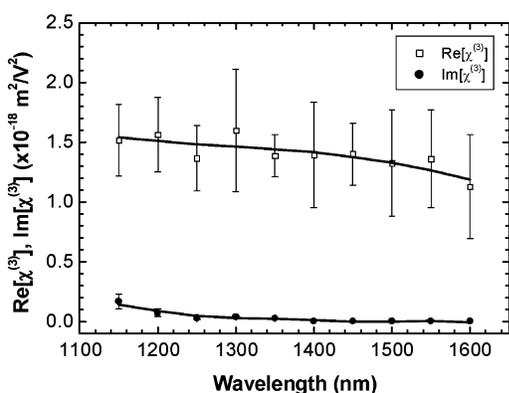
Figure 2. Spectra of real part Re[$\chi^{(3)}$] and imaginary part Im[$\chi^{(3)}$] of the third-order NLO susceptibility of film **a**.

The $\chi^{(3)}$ of polymer films constitutes two parts: the real part (Re[$\chi^{(3)}$]) and imaginary part (Im[$\chi^{(3)}$]) that are related to n_2 and β, respectively. The spectra of (Re[$\chi^{(3)}$]) and (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 Re[$\chi^{(3)}$], falls in the range of $(1.13-1.54) \times 10^{-18}$ m^2 V^{-2} and at 1550 nm is 1.36×10^{-18} m^2 V^{-2} (9.74×10^{-11} esu). Film **b** has a $\chi^{(3)}$ value of 2.61×10^{-19} m^2 V^{-2} (1.87×10^{-11} esu) at 1550 nm. The γ values for the C$_{60}$ moiety in films **a** and **b** are determined to be 9.6×10^{-32} and 1.7×10^{-32} esu at 1550 nm, respectively. In comparison with other C$_{60}$ materials (Table 1), C$_{60}$−PU films display the largest $\chi^{(3)}$ value, typically in 1−2 orders of enhancement over recently reported C$_{60}$ materials. The γ values are also larger than other C$_{60}$ derivatives and polymers.[3] 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 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 1.9×10^{20} cm^{-3}) of C$_{60}$ into a highly cross-linked polymer. A strong charge-transfer process in which C$_{60}$ 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 γ 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$_{60}$-PU Films with Other C$_{60}$ Materials[a]

materials [ND]	$\chi^{(3)}$, esu (wavelength)	γ, esu
C$_{60}$ solution[5a,b] [$(4.2-16.2) \times 10^{18}$]	5.8×10^{-15} (452 nm)	3.7×10^{-35}
C$_{60}^-$ solution[5a,b] [$(0.8-2.7) \times 10^{18}$]	N/A (452)	2.4×10^{-33}
C$_{60}$(NH$_2$CN)$_5$ solution[5c] [1.8×10^{18}]	5.8×10^{-14} (830 nm)	1.0×10^{-32}
C$_{60}$-silane sol−gel[5d] [9.6×10^{17}]	1.4×10^{-13} (820 nm)	not available
C$_{60}$-PSt solution[5f] [3.9×10^{18}]	1.1×10^{-12} (800 nm)	6.6×10^{-32}
C$_{60}$ film[5h] [1.3×10^{21}]	9.6×10^{-12} (1830 nm)	4.3×10^{-34}
C$_{60}$-PU film **a** [1.9×10^{20} (this work)]	9.7×10^{-11} (1550 nm)	9.6×10^{-32}

[a] ND = number density of C$_{60}$ moiety (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$_{60}$-PU films. The availability of a wide range of functionalized C$_{60}$ and C$_{60}$/polymer formulations opens a viable route to further development of suitable materials for all-optical switching devices.

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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