[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.1 To be practically useful for all-optical switching, materials should have a large nonlinear refractive index (n2) 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 (C60).4 Furthermore, when double bonds are broken and an electron donor group is attached, C60 derivatives show prominent enhancement in molecular second hyperpolarizability γ, as compared with pristine C60.5 To realize the large third-order NLO susceptibility (χ(3)) of C60 derivatives in a device, it is necessary to have a relatively thick, homogeneous film containing a high loading of C60 derivative and to preserve the high γ per C60 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 3OH-C60. The reported method is advantageously simple for preparation of high-quality C60 polymer films and also practically adaptable for making other NLO polymeric films.

C60 was first functionalized using the well-established 1,3-dipolar cycloaddition of azomethine which is derived from an α-amino acid and an aldehyde.5 A trihydroxyl-containing C60 (3OH-C60) was prepared in good yield from C60, tricine, and benzaldehyde and was purified by chromatography. The cyclic amine moiety in 3OH-C60 is expected to contribute to the required charge transfer, and the hydroxyl groups are used for cross-linking with an isocyanate. In comparison with C60, 3OH-C60 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 3OH-C60 (Scheme 1). Both films a and b contain 25 wt % of 3OH-C60 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 C60 moiety around 330 nm for films a and b, 3OH-C60 and pristine C60, which is known to become broad with a tail close to 700 nm for the substituted C60.6 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.

The nonlinear refractive index or Kerr coefficient (n2) and nonlinear absorption coefficient (β) for the C60-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...
wavelength interval of 50 nm. The Z-scan setup and data interpretation can be found elsewhere. At 1550 nm, no valley or peak in the open-aperture curve is observed for film a, indicating that no nonlinear absorption exists (α = 0). Its Kerr coefficient n2 is measured to be positive, (2.0 ± 0.6) × 10⁻³ cm²/GW. For polymer film b, the n2 value is (3.7 ± 0.8) × 10⁻⁴ cm²/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 = nβα and T = βlnn2, where I is the intensity of the incident light, α0 is one-photon absorption, and λ is the wavelength of the light, it is necessary to achieve W ≫ 1 and T ≪ 1 for any materials to be practically useful for all-optical switching. Because the C60-PU films exhibit negligible one-photon absorption (α0) throughout the region of 1150–1600 nm, the W value should be ideal, that is, W ≫ 1. The T value near 1150 nm is marginal due to a nonlinear absorption at the wavelengths near 1550 nm, but satisfactory near 1550 nm. Therefore, C60-PU materials are deemed to be suitable for device applications at the NIR wavelengths.

The χ³ of polymer films constitutes two parts: the real part (Re[χ³]) and imaginary part (Im[χ³]) that are related to n2 and β respectively. The spectra of (Re[χ³]) and (Im[χ³]) of film a derived from the experimental results are shown in Figure 2. The χ³ value of film a, mostly contributed from Re[χ³], falls in the range of (1.13–1.54) × 10⁻¹⁸ m² V⁻² and at 1550 nm is 1.36 × 10⁻¹⁸ m² V⁻² (9.74 × 10⁻¹¹ esu). Film b has a χ³ value of 2.61 × 10⁻¹⁹ m² V⁻² (1.87 × 10⁻¹¹ esu) at 1550 nm. The χ values for the C60 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 C60 materials (Table 1), C60-PU films display the largest χ³ value, typically in 1–2 orders of enhancement over recently reported C60 materials. The χ³ values are also larger than other C60 derivatives and polymers. The observed large χ³ 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[χ³] 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 case is believed to be mainly due to the successful incorporation and well dispersion of large amount (19.1 wt % or the number

\[ \begin{align*}
\chi^{(3)}(\text{polymer films}) &= \chi^{(3)}(\text{film a}) \approx 2.61 \times 10^{-19} \text{ m}^2 \text{ V}^{-2} \quad \text{(at 1550 nm)} \\
\chi^{(3)}(\text{film b}) &= 9.6 \times 10^{-32} \text{ esu} \quad \text{(at 1550 nm)}
\end{align*} \]

Table 1. Comparison of Third-Order Optical Nonlinearity of C60-PU Films with Other C60 Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>χ³, esu (wavelength)</th>
</tr>
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<tbody>
<tr>
<td>C60 solution</td>
<td>5.8 × 10⁻¹⁵ (452 nm)</td>
</tr>
<tr>
<td>C60™ solution</td>
<td>N/A</td>
</tr>
<tr>
<td>C60(NH4CN)3 solution</td>
<td>5.8 × 10⁻¹⁴ (830 nm)</td>
</tr>
<tr>
<td>C60-silane–gel®</td>
<td>1.4 × 10⁻¹³ (1820 nm)</td>
</tr>
<tr>
<td>C60-PST solution</td>
<td>1.1 × 10⁻¹² (1000 nm)</td>
</tr>
<tr>
<td>C60 film</td>
<td>9.6 × 10⁻¹² (1830 nm)</td>
</tr>
<tr>
<td>C60-PU film</td>
<td>9.7 × 10⁻¹¹ (1550 nm)</td>
</tr>
</tbody>
</table>

*ND = number density of C60 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 C60-PU films. The availability of a wide range of functionalized C60 and C60/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.

References