Ultrafast nonresonant third-order optical nonlinearity of fullerene-containing polyurethane films at telecommunication wavelengths

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High-optical-quality polyurethane films containing a high load of (60)fullerene (C_{60}) were prepared by reaction of the hydroxy-containing C_{60} and triisocyanate with the goal of obtaining enhanced nonresonant third-order optical nonlinearity. Optical nonlinearity was measured using the Z-scan technique in the wavelength range 1150–1600 nm. This revealed a positive Kerr coefficient with nonresonant n_2 equal to $2.0(\pm 0.6)\times 10^{-3}$ cm^2/GW and excellent linear-absorption and nonlinear-absorption figures of merit at 1550 nm. The technique reported herein is a new approach to obtain fullerene films with the capacity to realize a high number density of C_{60} moieties. These resulted in more than 2 orders of enhancement in the third-order susceptibility over recently reported C_{60} sol and gel, and an enlarged second-order hyperpolarizability resulting from further enhanced charge transfer processes. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1609660]

Third-order nonlinear optical (NLO) phenomena of conjugated organic compounds and polymers are of great interest in optical switching and signal processing for their large optical nonlinearity and fast response time.[1–6] However, few organic materials reported to date provide suitable nonlinearity (large nonresonant nonlinearity with response time of picoseconds or less) in the near infrared region.

The nonlinear refractive index n_2 ($n=n_0+n_2I$, where n_0 is the linear part of the refractive index and I the incident intensity) may be enhanced through one- or two-photon resonant transitions. These are accessed when the absorption peak wavelength of the material lies sufficiently close to one or half of the operating wavelength. However, this resonant enhancement of n_2 is accompanied by optical loss due to absorption, described by $\alpha=\alpha_0+\beta I$, where α_0 is the linear absorption coefficient and β is the nonlinear absorption coefficient. The NLO efficiency/transparency tradeoff (n_2/α) at a specific wavelength is therefore of primary importance for assessing the suitability of a material for use in a device. This parameter is usually evaluated through two figures of merit: $W=n_2I/\alpha_0\lambda$ and $T=\beta\lambda/n_2$. According to the requirements mentioned above, it is necessary to achieve $W \gg 1$ and $T \ll 1$.

Fullerenes (e.g., C_{60}), a class of highly conjugated compounds, have attracted considerable research interest for their large and fast optical nonlinearities.[7–12] Owing to the large activity of C_{60} molecules with an abundance of delocalized π electrons, the synthesis of chemically modified C_{60} derivatives has been used to improve the solubility of C_{60} in solution with the hope of achieving a strong NLO response.[8,9,12] Previous research has been performed on C_{60} in solution. The nonlinear optical properties of fullerenes and their derivatives in solid-state films have not been well studied due to the difficulties in obtaining homogeneously mixed fullerene molecules in a matrix.[10–12]

In this study, a high-quality film of crosslinked polyurethane containing a high content of covalently bonded C_{60} is studied using the Z-scan technique. The material was designed to achieve significant charge transfer with a high C_{60} concentration while retaining the highly delocalized π electrons of C_{60} and good film-forming ability. This article reports on the third-order optical nonlinearity of fullerene derivatives cast into films in the wavelength range of 1150–1600 μm.

Trihydroxyl-containing C_{60} ($3OH–C_{60}$) was prepared with high yield and characterized by IR and UV-Vis-NIR spectroscopic methods.[13] The hydroxyl groups in $3OH–C_{60}$ can react with a triisocyanate compound, resulting in a crosslinked C_{60}-containing polyurethane system (Fig. 1). Film formation and subsequent thermal cure were carried out as follows: 0.06 g of TMP (a triisocyanate derived from trimethylolpropane and xylylene diisocyanate) was mixed with 0.02 g of $3OH–C_{60}$ in 0.3 mL of 1-methyl-2-pyrolidinone (NMP) at room temperature resulting in a $3OH–C_{60}$ concentration of 25 wt % (19.1 wt % for C_{60} moieties). After filtering through a microfilter (pore size: 0.2 μm), the solution

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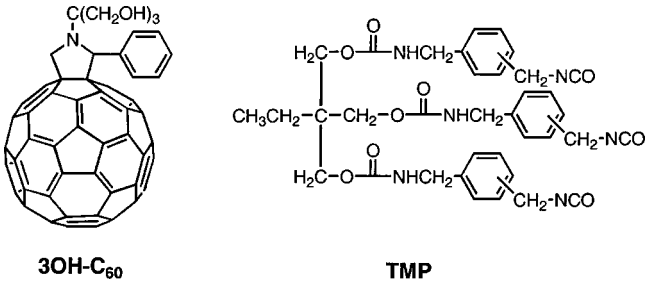

FIG. 1. Hydroxy-containing C_{60} ($3OH-C_{60}$) and triisocyanate (TMP) used for preparation of crosslinked C_{60}-containing polyurethane films.

was cast on glass plates. After drying overnight at 50 °C under a nitrogen flow, the films were cured through the following heating steps: 1 h at 120 °C, 1 h at 160 °C, and then 30 min at 210 °C. comparison of the absorption spectra of the film (thickness of 29.54 μm) and pristine C_{60} (Aldrich, 99.5%) in toluene in the visible and near-infrared regions shows that the film possesses a broader absorption peak with a tail close to 700 nm while the pristine C_{60} in solution absorbs within the range of 270–400 nm. It is known that C_{60} derivatives show weak or no characteristic absorption (λ_{max} 330 nm) of pristine C_{60}, depending on the degree of substitution.[14]

The tunable laser for the measurement came from a picosecond Ti:sapphire amplified system with an optical parametric amplifier (Fig. 3), which produced output at pulsewidth 3.3 ps and repetition rate 1 kHz. The description of the laser system and the measuremnet can be found elsewhere.[15–17] Figure 2 shows the spectra of n_2 and β in the wavelength range 1150–1600 nm measured consecutively at a wavelength interval of 50 nm. At 1550 nm, the open-aperture curve does not show any valley or peak indicating that no nonlinear absorption exists ($\beta=0$). Fitting with $\Delta\Phi_0$ and z_0 as variables yields $\Delta\Phi_0=0.43$ and $z_0=1.2$ mm. Following the relation $\Delta\Phi_0=2\pi\Delta nL_{\text{eff}}/\lambda$, it is possible to obtain the refractive index change at the focal point $\Delta n=3.6\times10^{-3}$ and Kerr coefficient $n_2=2.0(\pm0.6)\times10^{-3}$ cm^2/GW. In this wavelength region, the n_2 values lie between $(1.6 \text{ and } 2.4)\times10^{-3}$ cm^2/GW while the β values decrease from about 20 cm/GW near 1150 nm to essentially zero at wavelengths above 1400 nm. Nonlinear absorption in the wavelength range 1150–1400 nm is attributable to multiphoton processes. Since the material exhibits negligible one-photon absorption α_0 throughout this infrared region, the W values are ideal, i.e., $W\gg1$. Due to nonlinear absorption at the wavelengths near 1150 nm, the T values near 1150 nm are marginal. However, T values are satisfactory near 1550 nm (see inset in Fig. 2).

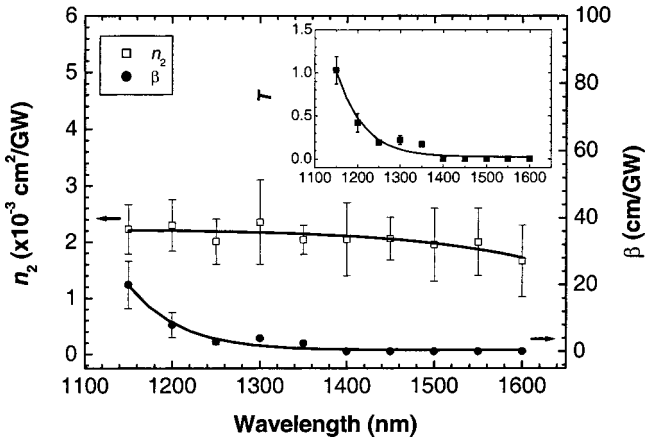

FIG. 2. Spectra of nonlinear refractive index n_2 and nonlinear absorption β of the film in the wavelength range of 1150–1600 nm. The inset shows the spectrum of the figure of merit T in the corresponding wavelength range. Solid lines are the viewing guides.

The nonlinear refractive index and nonlinear absorption coefficient are related to the real part ($\text{Re}[\chi^{(3)}]$) and imaginary part ($\text{Im}[\chi^{(3)}]$) of the third-order nonlinear optical susceptibility through the equations[2,17]

$$\text{Im}[\chi^{(3)}]=\frac{2\varepsilon_0c^2n_0^2}{3\omega}\beta, \tag{1}$$

$$\text{Re}[\chi^{(3)}]=\varepsilon_0cn_0^2n_2, \tag{2}$$

$$\chi^{(3)}=\text{Re}[\chi^{(3)}]+i\,\text{Im}[\chi^{(3)}], \tag{3}$$

where c is the speed of light in vacuum, and ε_0 is the permittivity of free space. n_2, β, and $\chi^{(3)}$ in these equations are in SI units with the units of m^2 W^{-1}, m/W, and m^2 V^{-2}, respectively. The calculated $\chi^{(3)}$ values, mostly contributed from $\text{Re}[\chi^{(3)}]$, fall in the range of $(1.13-1.54)\times10^{-18}$ m^2 V^{-2} with a value of 1.36×10^{-18} m^2 V^{-2} (9.74×10^{-11} esu) at 1550 nm.

The molecular second-order hyperpolarizability γ in isotropic media is related to $\chi^{(3)}$ by

$$\gamma=\frac{\chi^{(3)}}{NL}, \tag{4}$$

where N is the number density of the molecule, and L is the local field correction factor, expressed as $[(n^2+2)/3]^4$ under the Lorentz–Lorenz approximation with the refractive index n. Using Eq. (4), we may estimate the value of γ for C_{60} moieties. From the measured refractive index of 1.60 and the calculated number density of 1.9×10^{20} cm^{-3}, the γ value for the C_{60} moieties in our sample is $\sim9.6\times10^{-32}$ esu at 1550 nm, which is 2.7 times the γ value of $C_{60}[(NH_2)_2CNCN]_5$ solution (3.5×10^{-32} esu) and 9.6 times the value of $C_{60}(NH_2CN)_5$ solutions (1.0×10^{-32} esu).[9]

Since C_{60} possesses regularly alternated hexagonal and pentagonal rings and poorly delocalized symmetric double bonds, its highly symmetric structure blocks most of transition pathways from the ground state to the excited states. By breaking double bonds and attaching an electron donor group, the C_{60} derivatives, with the alternated electron symmetry of C_{60} molecules by the introduced electrons, show prominent enhancement on the optical nonlinearity, as compared with pristine C_{60}. The mechanism for the significant enhancement in our case is believed to be due to a strong charge transfer process in which C_{60} moiety acts as an electron acceptor and the substitute group or polymeric host serves as an electron donor. Reported techniques on the incorporation of C_{60} in solid state have been mainly focused on the doping into glasses or sol-gel techniques. However, restricted by crack formation at higher C_{60} concentration (~0.1 wt %), the feasible doping levels reported were quite low (0.01–0.1 wt %).[11] The successful incorporation of large amount (19.1 wt %) of C_{60} moieties into a highly

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TABLE I. Comparison of third-order optical nonlinearity of C_{60}-containing polyurethane film in this study with previous studies on C_{60} derivatives.

Reference and measurement wavelength	Material	Concentration	Number density (cm^{-3})	$\chi^{(3)}$ (esu)	γ (esu)
Ref. 8 (~452 nm)	Neutral species solution	7–27 mM	$(4.2–16.2)\times10^{18}$ (ca.)	$<5.8\times10^{-15}$	$<3.7(\pm1.5)\times10^{-35}$ (ca.)
	Anionic C_{60} solution	1.3–4.5 mM	$(0.8–2.7)\times10^{18}$ (ca.)	—	$2.4(\pm1.0)\times10^{-33}$
Ref. 9 (830 nm)	$C_{60}(NH_2CN)_5$ solution	3 mM	1.8×10^{18} (ca.)	5.8×10^{-14}	1.0×10^{-32}
	$C_{60}[(NH_2)_2CNCN]_5$ solution	1.0 mM	6.0×10^{17} (ca.)	6.8×10^{-14}	3.5×10^{-32}
Ref. 12 (820 nm)	C_{60}-silane sol	1.6 mM	9.6×10^{17} (ca.)	1.4×10^{-13}	—
	C_{60}-silane gel	1.6 mM	9.6×10^{17} (ca.)	1.6×10^{-13}	—
This study (1550 nm)	Crosslinked C_{60}-polyurethane film	19.1 wt %	1.9×10^{20}	9.7×10^{-11}	9.6×10^{-32}

(ca.), data calculated from the information in the references; —, data unavailable.

crosslinked polymeric system achieving a high number density of C_{60} moieties is crucial to realize the significant increase of $\chi^{(3)}$ values in this study over those of charge-transferred C_{60} reported elsewhere.[7–12] A comparison of the third-order optical nonlinearity obtained in this study with previous studies is given in Table I. It is shown that the $\chi^{(3)}$ value of C_{60}-containing polyurethane film herein provides a more than 2 orders of magnitude enhancement over recently reported C_{60}–siliane sol and gel. The discrepancy in the values of γ between our measurements and those reported previously comes mainly from the different behaviors of electron donors, which result in the different extents of the charge transfer processes. It was reported that it is possible for the magnitude of $\chi^{(3)}$ for C_{60} with different electron donors to vary near one order magnitude.[12] One of the starting materials ($3OH–C_{60}$) in our synthesis before crosslinking process was trihydroxyl-containing C_{60}, which was a charge transfer C_{60} complex with similar molecular structures as the charge transfer C_{60} complexes reported previously. Our crosslinking process is a new technique, which realizes a high number density of C_{60} moieties, further enhance the charge transfer processes of the materials, and render the possibility to fabricate high-quality uniform films. We believe the enhanced charge transfer processes with crosslinking in this study accounts for the enhancement of γ values. Our results confirmed some foresights of Lascola *et al.* that $C_{60}^{-}\chi^{(3)}$ can be optimized by derivatization, choice of matrix, and reduction to lower valence states, and charged fullerenes can have bulk nonlinearities that are comparable to the best organic materials,[8] for example, polydiacetylene-based polymer PTS (p-toluene sulfonate) ($\chi^{(3)}=5\times10^{-10}$ esu)[18] and recently reported single-crystal PTS [$n_2=2.2(\pm0.3)\times10^{-12}\sim5(\pm1)\times10^{-12}$ cm^2/W].[6,19]

In summary, third-order optical nonlinearity of conjugated crosslinked C_{60}-containing polyurethane films with the enhancement of nonlinearity by the charge transfer process is investigated and found to possess ultrafast nonresonant nonlinearity around 1550 nm with excellent figures of merit. Molecular engineering is effective in manipulating the optical properties of the materials and overcoming the low solubility of pristine C_{60} to fabricate high-quality films with high number density of C_{60} moieties. It results in large third-order susceptibility and the second-order hyperpolarizability from the enhanced charge transfer processes via crosslinking. The spectral dependence of the third-order optical nonlinearity over a wide infrared wavelength range informs structure-property relationships,[20] and in the range 1300–1600 nm, is pertinent to applications in optical signal processing in communication systems.

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