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Optical Limiting Properties of [60]Fullerene and Methano[60]fullerene Derivative in Solution versus in Polymer Matrix: The Role of Bimolecular Processes and a Consistent Nonlinear Absorption Mechanism

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Optical limiting properties of *tert*-butyl methano[60]fullerene carboxylate were investigated systematically in room-temperature solution at a series of concentrations while the linear transmittance of the solution at 532 nm was kept constant. The results are compared with those of [60]fullerene (C_{60}) obtained under the same experimental conditions. For both C_{60} and the methano-C_{60} derivative, optical limiting responses toward the second harmonic of a Q-switched Nd:YAG nanosecond pulsed laser at 532 nm are strongly dependent on the fullerene solution concentrations. The concentration dependence is not related to any special optical effects because the results of chloroaluminum phthalocyanine as a reference in the optical limiting experiments show no such dependence. Instead, the strong concentration dependence in the optical limiting performance of fullerenes in solution is likely due to concentration effects on optical limiting contributions that are associated with bimolecular excited-state processes in the fullerenes. For an examination of the medium viscosity dependence of the bimolecular excited-state processes, optical limiting responses of the methano-C_{60} derivative in highly viscous nonreactive solvent−polymer blends were determined and compared with those in solution at the same linear transmittances. The optical limiting responses are significantly weaker in the highly viscous media, consistent with medium viscosity effects on diffusional or pseudodiffusional bimolecular excited-state processes. Also consistent with such effects are the results that optical limiting responses of the methano-C_{60} derivative in poly(methyl methacrylate) polymer films are much weaker than those in room-temperature solution. A reverse saturable absorption mechanism that includes both unimolecular and bimolecular (self-quenching and triplet−triplet annihilation) excited-state processes of fullerenes is proposed. A consistent understanding of the optical limiting properties of fullerenes in room-temperature solution (including the strong concentration dependence), in a highly viscous solvent−polymer blend, and in polymer film is discussed within a single mechanistic framework.

Introduction

The development of modern optical technology for all-optical, electro-optical, acousto-optical, and optomechanical devices demands the ability to control the intensity of light in a predetermined and predictable manner.[1−3] There is great current interest in organic and inorganic nonlinear optical materials for potential optical switching and passive-mode optical limiting applications. An ideal optical limiter exhibits linear transmission below a certain input light fluence threshold, but above the threshold, the output light fluence becomes constant at a fixed level.[1a] Among the most promising optical limiters under active investigations are materials showing strong nonlinear absorptions, which are commonly referred to as reverse saturable absorbers.[1−7] The primary mechanism for the nonlinear absorptive optical limiting is a large ratio of excited-state to ground-state absorption cross sections. Thus, potent reverse saturable absorbers are typically molecules with weak ground-state absorptions, such as metallophthalocyanines,[5,6] mixed metal complexes and clusters,[8] and fullerenes.[7,9−21]

Since Tutt and Kost first reported[7] that [60]fullerene (C_{60}) in toluene solution is an excellent optical limiter toward a nanosecond pulsed Nd:YAG laser at 532 nm, there have been extensive investigations of fullerene optical limiting properties.[9−21] The optical limiting performance of C_{60} in solution was reported to be concentration independent, though the experimental results on which the report was based apparently contain large uncertainties.[16] For C_{60} in room-temperature toluene solution, McLean et al. used a five-level model for reverse saturable absorption (Figure 1) to correlate the observed optical limiting responses with the ground- and excited-state absorption cross sections of C_{60}.[9] Similar correlations were performed by several other groups.[12,13] For optical limiting toward a nanosecond pulsed laser at 532 nm, it was concluded[9] that the C_{60} results in room-temperature toluene solution follow the five-level model for input light fluences of up to ∼1 J/cm^2 and that the optical limiting is due predominantly to the strong triplet−triplet absorption of C_{60}. Despite the excellent correlation of experimental optical limiting results with the five-level model (Figure

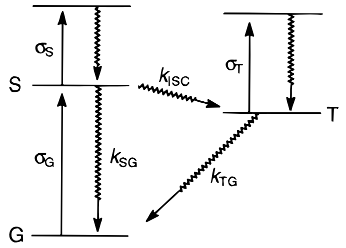

Figure 1. Five-level reverse saturable absorption model.

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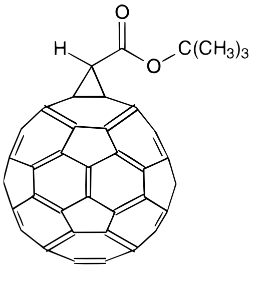
1),[9,12,13] which may be regarded as strong evidence for reverse saturable absorption, mechanistic details on the optical limiting properties of fullerenes remain a subject of debate. Significant contributions from other nonlinear optical processes, such as nonlinear scattering,[11,21] have been suggested. Important experimental evidence for possible contributions from mechanisms other than reverse saturable absorption includes the observation that the optical limiting performance of fullerenes in solid matrixes is rather different from that in solution.[17−21] For example, it was reported that the optical limiting responses of C_{60} dispersed in a poly(methyl methacrylate) (PMMA) matrix are much weaker than those in room-temperature toluene solution.[21] The dramatic difference in the optical limiting performance of C_{60} from solution to PMMA matrix cannot be attributed to changes in the nonlinear absorptive behavior because the ground-state and triplet−triplet transient absorption spectra of C_{60} in PMMA polymer film are similar to those in room-temperature toluene solution.[22a] Thus, it is a strong possibility that the optical limiting properties of C_{60} in solution and in solid matrix are in fact dominated by different mechanisms or mechanistic processes.

Here, we report a systematic investigation of the optical limiting properties of C_{60} and *tert*-butyl methano-C_{60} carboxylate in room-temperature toluene solutions of different concentrations (a variation of 2 orders of magnitude), in PMMA polymer films, and in highly viscous solvent−polymer blends. Chloroaluminum phthalocyanine was used as a reference for optical limiting measurements under the same experimental conditions as those used for the fullerenes. The results show that the optical limiting responses of both C_{60} and the methano-C_{60} derivative in room-temperature solution toward nanosecond laser pulses at 532 nm are strongly dependent on the fullerene solution concentrations, which suggests significant optical limiting contributions that are related to bimolecular excited-state processes of the fullerenes. The results also show that the optical limiting performance of the fullerenes is significantly affected by changes in the medium viscosity, which may be understood in terms of medium viscosity effects on bimolecular excited-state processes that are diffusional or pseudodiffusional in nature. Mechanistic implications of the experimental results are discussed, and a reverse saturable absorption model that consistently accounts for the optical limiting properties of fullerenes in both solution and a solid matrix is proposed.

Experimental Section

Materials. C_{60} was obtained from Southern Chemical Group (purity >99.5%). The sample purity was checked by UV−vis absorption, ^{13}C NMR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS methods, and the sample was used without further purification. The methano-C_{60} derivative **I** was prepared by use of the reaction of C_{60} with the stabilized sulfonium ylide.[23,24] Briefly, the one-pot preparation was carried out under a phase-transfer condition. A toluene solution of C_{60}, *tert*-butyl bromoacetate sulfonium salt, K_2CO_3, and the phase-transfer catalyst tetrabutylammonium bromide (TBAB) was mixed and reacted at room temperature. The stabilized sulfonium ylide generated in situ due to the deprotonation of the sulfonium salt by K_2CO_3 under the catalysis of TBAB undergoes nucleophilic addition to C_{60}, followed by intramolecular substitution to form the methano-C_{60} derivative **I** with a simultaneous elimination of dimethyl sulfide. The compound **I** was positively identified by NMR and MALDI-TOF MS methods.

Chloroaluminum phthalocyanine **II** was purchased from Exciton Inc. and used without further purification. Poly(methyl methacrylate) (PMMA) polymer of average molecular weight M_w of ∼315 000 was purchased from Acros Organics, and poly(propionylethyleneimine) (PPEI) polymer of average molecular weight M_w of ∼500 000 was purchased from Aldrich. Both polymer samples were used as received. Spectrophotometry grade toluene and chloroform were obtained from Burdick & Jackson, and dimethylformamide (DMF) was obtained from Mallinckrodt. The solvents were used as received.



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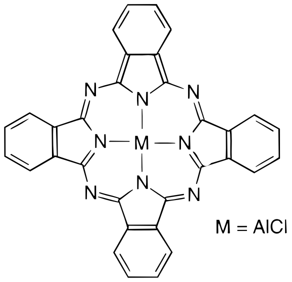

II

Measurements. Absorption spectra were recorded on a computer-controlled Shimadzu UV2101-PC spectrophotometer. Solution samples were measured in glass or quartz cuvettes, and the results were corrected for surface losses. Absorption spectra of free-standing polymer films were measured by placing the films in a polyethylene sample holder on a fixed stand.

Triplet−triplet transient absorption spectra were obtained using a laser flash photolysis setup. The excitation source of the setup is the third harmonic from a Continuum Surelite-I Q-switched Nd:YAG laser (355 nm, 4 ns pulse width, 10 Hz repetition). The probing light source is a 450 W xenon arc lamp through a water filter and a mechanical shutter from Vincent Associates, which is synchronized with the laser excitation pulse by use of a timing control unit made in house. The wavelength of probing light is selected through a Spex 1681B monochromator. The detector consists of a Hamamatsu R928 photomultiplier tube, a Stanford Research Systems SR455 amplifier, and a Tektronix TDS-350 digital oscilloscope interfaced to a personal computer. In transient absorption measurements, the signals were averaged over 250 laser shots to improve the signal-to-noise ratio.

The experimental setup for optical limiting measurements consists of a Continuum Surelite-I Q-switched Nd:YAG laser operated in the single-shot mode. The second harmonic from frequency doubling the infrared fundamental is isolated by use of the Surelite harmonic separation package. The laser beam is collimated, with the maximum energy of 160 mJ/pulse at 532 nm and a 5 ns pulse width (fwhm). The laser pulse energy is varied in the range of 10−160 mJ/pulse using a waveplate−polarizer combination. With the laser beam diameter of 6 mm, the corresponding input energy densities for optical limiting measurements are in the range of 0.035−0.57 J/cm^2. For higher energy densities of up to 2.2 J/cm^2, the laser beam diameter is reduced to 3 mm using a galilean style telescope, which consists of a planoconcave lens and a planoconvex lens. The detector is a Scientech Mentor MC2501 calorimeter controlled by a Scientech MD10 meter. For solution samples of different concentrations, optical limiting measurements were carried out using cuvettes of different optical path lengths. The film samples were measured by placing the films in a polyethylene sample holder on a fixed stand.

Results

Ground-State Absorption. The ground-state absorption spectrum of the methano-C_{60} derivative **I** in toluene at room

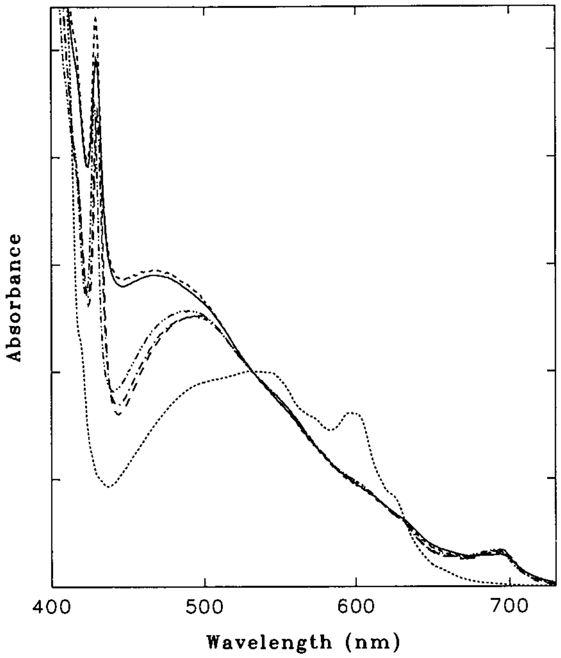

Figure 2. Absorption spectra of the methano-C_{60} derivative **I** in room-temperature toluene (— —), toluene−PMMA (-•-), and chloroform−PPEI (-••-) polymer blends and thin (---) and thick (—) PMMA polymer films. The spectrum of C_{60} in toluene (•••) is also shown for comparison.

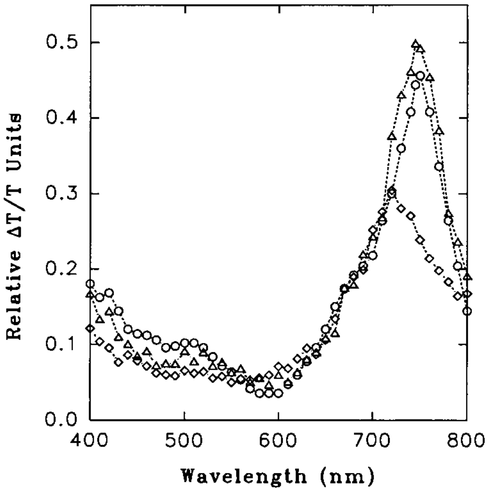

Figure 3. Triplet−triplet absorption spectrum of the methano-C_{60} derivative (◆) is compared with those of C_{60} (△) this work and (○) ref 26).

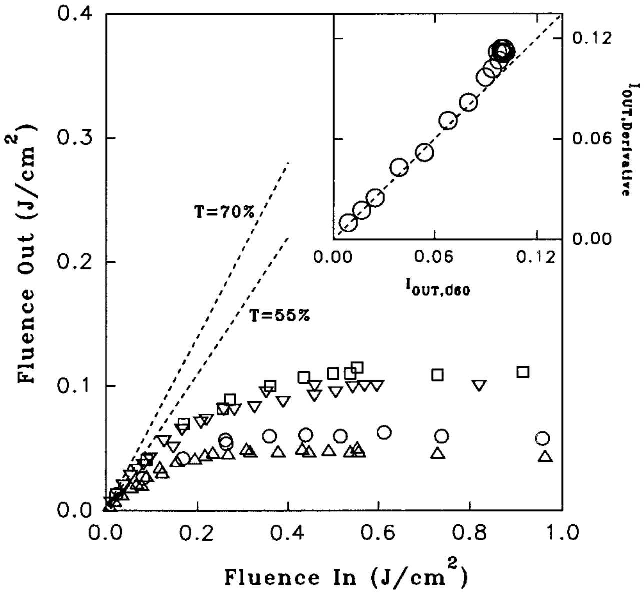

Figure 4. Optical limiting responses of C_{60} and the methano-C_{60} derivative **I** in room-temperature toluene solutions of 55% (C_{60} (△); **I** (○)) and 70% (C_{60} (▽); **I** (□)) linear transmittances at 532 nm. Shown in the inset is a plot of the output light fluences for the derivative vs those for C_{60} at the same input light fluences and the same linear transmittance of 70% at 532 nm.

temperature (22 °C) is shown in Figure 2. The spectrum is noticeably different from that of C_{60}. The weak absorption band at ~695 nm is characteristic of C_{60} derivatives.[25] At 532 nm, the molar absorptivity of the derivative is 1250 M^{-1} cm^{-1} (cross section σ_G of 4.78×10^{-18} cm^2), larger than that of C_{60} (940 M^{-1} cm^{-1}, cross section σ_G of 3.59×10^{-18} cm^2).

Excited Triplet-State Absorption. Triplet−triplet absorption spectra were measured using the nanosecond laser flash photolysis method. Sample solutions for the measurements were carefully degassed under high vacuum (5×10^{-5} Torr) with up to 14 freeze−pump−thaw cycles. For calibration, the triplet−triplet absorption spectrum of C_{60} in room-temperature toluene was recorded and compared with the spectrum reported in the literature.[22ab] As shown in Figure 3, the agreement with the literature result is excellent.

For the methano-C_{60} derivative **I**, a toluene solution with an optical density of ~1 at the excitation wavelength 355 nm was used in the measurement. The triplet−triplet absorption spectrum of the derivative has a profile similar to that of C_{60}, but it is blue shifted ~25 nm. The spectrum is similar to triplet−triplet absorption spectra of other methano-C_{60} derivatives.[25,27] In general, the triplet−triplet absorption of the derivative **I** is weaker than that of C_{60} (Figure 3). The molar absorptivities at the spectral maxima are ~12 200 M^{-1} cm^{-1} (cross section σ_T of 4.67×10^{-17} cm^2) at 720 nm for the derivative **I** and ~19 500 M^{-1} cm^{-1} (cross section σ_T of 7.46×10^{-17} cm^2) at 745 nm for C_{60} in room-temperature toluene.[26,27] However, at 532 nm, the triplet−triplet absorptivities of the derivative **I** and C_{60} are comparable, on the order of 4200 M^{-1} cm^{-1} (cross section σ_T of 1.6×10^{-17} cm^2).[26,27]

Optical Limiting in Solution, Derivative vs C_{60}. Optical limiting properties of the methano-C_{60} derivative **I** were investigated to compare the results with those of C_{60}. Shown in Figure 4 are optical limiting responses of the derivative in toluene solutions of 55% and 70% linear transmittances in a cuvette with a 2 mm optical path length. The output fluences (I_{OUT}) are first linear with input fluences (I_{IN}) and then level off and reach a plateau at high input fluences (Figure 4). The saturated I_{OUT} values at the plateau are 0.06 and 0.11 J/cm^2 for solutions (2 mm optical path length) of 55% and 70% linear transmittances, respectively. The results are the same as those of other methano-C_{60} derivatives[14a−c] and similar to those of the parent C_{60} in room-temperature toluene (Figure 4). Shown in the inset of Figure 4 is a more direct comparison of the optical limiting results between the derivative and the parent C_{60}. The I_{OUT} values of the derivative are plotted against those of C_{60} at the same I_{IN} values. The plot is close to the 45 degree line, indicating close similarity in optical limiting responses between the methano-C_{60} derivative **I** and the parent C_{60}.

Optical Limiting in Solution, Concentration Dependence. The optical limiting responses of the methano-C_{60} derivative **I** were measured systematically in a series of toluene solutions of different concentrations. To keep the linear transmittance constant, a series of cuvettes with different optical path lengths from 1 to 100 mm were used. At a constant linear transmittance

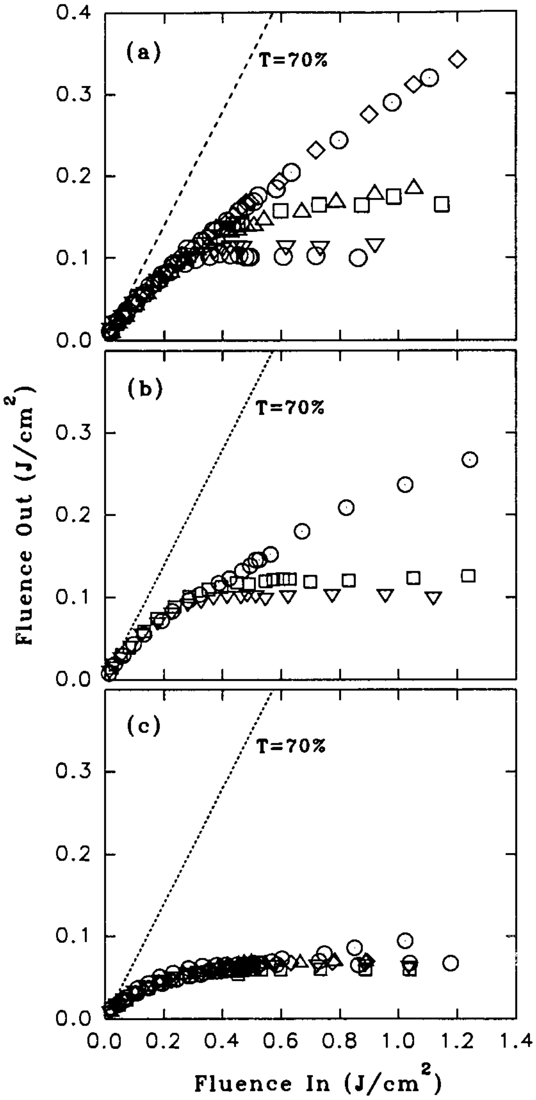

Figure 5. Optical limiting responses of (a) the methano-C_{60} derivative **I** and (b) C_{60} in toluene and (c) chloroaluminum phthalocyanine **II** in DMF at room temperature. At a constant linear transmittance of 70% at 532 nm, the solution concentration decreases with the optical path length (○) 1 mm, (◇) 2 mm, (□) 10 mm, (△) 20 mm, (⊙) 50 mm, and (◆) 100 mm).

TABLE 1: Optical Limiting Properties of C_{60} and the Methano-C_{60} Derivative I in Solution and in Highly Viscous Solvent−Polymer Blends

c (M)	solvent	l (mm)[a]	T (532 nm)	I_{OUT} (J/cm²)[b]	T/T_0[b]
		C_{60}			
3.28×10^{-5}	toluene	50	70%	0.23_5	0.34
1.64×10^{-4}	toluene	10	70%	0.12	0.17
8.19×10^{-4}	toluene	2	70%	0.1	0.14
		Methano-C_{60} Derivative			
1.23×10^{-5}	toluene	100	70%	0.30_5	0.44
2.46×10^{-5}	toluene	50	70%	0.3	0.43
6.16×10^{-5}	toluene	20	70%	0.18	0.26
1.23×10^{-4}	toluene	10	70%	0.17	0.24
6.16×10^{-4}	toluene	2	70%	0.11	0.16
1.23×10^{-3}	toluene	1	70%	0.1	0.14
5.92×10^{-4} [c]	tol−PMMA[d]	2	71%	0.17	0.24
5.92×10^{-4}	toluene	2	71%	0.14	0.2
1.04×10^{-3} [c]	tol−PMMA[e]	2	55%	0.09	0.16
1.04×10^{-3}	toluene	2	55%	0.07	0.13
6.4×10^{-4} [c]	$CHCl_3$−PPEI[f]	2	69%	0.16	0.23
6.4×10^{-4}	toluene	2	69%	0.1	0.15

[a] Optical path length. [b] At I_{IN} = 1 J/cm². [c] Estimated with the assumption of the same molar absorptivity as in toluene. [d] Contains 0.25 g/mL of PMMA. [e] Contains 0.4 g/mL of PMMA. [f] Contains 0.3 g/mL of PPEI.

of 70%, solution concentrations were varied over 2 orders of magnitude, from 1.23×10^{-5} to 1.23×10^{-3} M. As shown in Figure 5a, the optical limiting results are clearly dependent on solution concentrations, with the changes particularly dramatic in the 2.46×10^{-5} to 6.16×10^{-5} M concentration range. At the highest concentration under consideration, 1.23×10^{-3} M, a cuvette with an optical path length of 1 mm was used. The concentrated solution exhibits strong optical limiting responses, reaching a plateau at an I_{IN} of ~0.35 J/cm². The saturated I_{OUT} value at the plateau is ~0.1 J/cm² (Figure 5a, Table 1). For solutions of lower concentrations, optical cells of longer path lengths were used in the measurements. While the result for the solution of 6.16×10^{-4} M (2 mm optical path length) is only slightly different from that of the most concentrated solution, the results of more dilute solutions (1.23×10^{-4} and 6.16×10^{-5} M with optical path lengths of 10 and 20 mm, respectively) are very different, with significantly larger saturated I_{OUT} values (Figure 5a, Table 1). At an even lower solution concentration of 2.46×10^{-5} M, corresponding to a longer optical path length of 50 mm, the solution exhibits optical limiting but reaches no plateau at input fluences I_{IN} up to 1.3 J/cm². The optical limiting responses of the low-concentration solution are generally much weaker than those of more concentrated solutions (Figure 5a). However, as the solution concentration decreases further to 1.23×10^{-5} M, corresponding to an even longer optical path length of 100 mm, there are hardly any further changes in the optical limiting result (Figure 5a, Table 1).

For comparison, similar experiments were carried out for C_{60} solutions of different concentrations. The results of C_{60} shown in Figure 5b are remarkably similar to those of the methano-C_{60} derivative **I**. At a constant linear transmittance of 70%, for example, the C_{60} solution in toluene of 8.2×10^{-4} M concentration (2 mm optical path length) exhibits strong optical limiting, reaching a plateau at an I_{IN} of ~0.35 J/cm² and having a saturated I_{OUT} value of ~0.1 J/cm² (Figure 5b, Table 1). However, the more dilute C_{60} solution of 1.6×10^{-4} M concentration (10 mm optical path length) again shows a plateau with a higher saturated I_{OUT} value of ~0.12 J/cm² (Figure 5b, Table 1). At an even lower C_{60} concentration of 3.3×10^{-5} M (optical path length of 50 mm), there is no optical limiting plateau at input light fluences up to 1.3 J/cm². The optical limiting responses of the dilute C_{60} solution are in general much weaker than those of the more concentrated C_{60} solutions, similar to that observed for the methano-C_{60} derivative **I** (Figure 5a,b, Table 1).

Optical Limiting in Solvent−Polymer Blends. For an examination of medium viscosity effects on optical limiting performance, highly viscous solutions of the methano-C_{60} derivative **I** in toluene-PMMA polymer ($M_w \approx 315\,000$) blends were prepared. The polymer blends, which contain 0.25−0.4 g/mL of PMMA polymer, serve as media of variable viscosities that are between those of room-temperature toluene solution and PMMA film. The absorption spectrum of the methano-C_{60} derivative **I** in toluene−PMMA polymer blends is essentially the same as that in room-temperature toluene solution (Figure 2). Optical limiting responses of the derivative in toluene−PMMA polymer blends were measured in a cuvette of 2 mm optical path length. As shown in Figure 6, the derivative exhibits noticeably weaker optical limiting responses in the highly

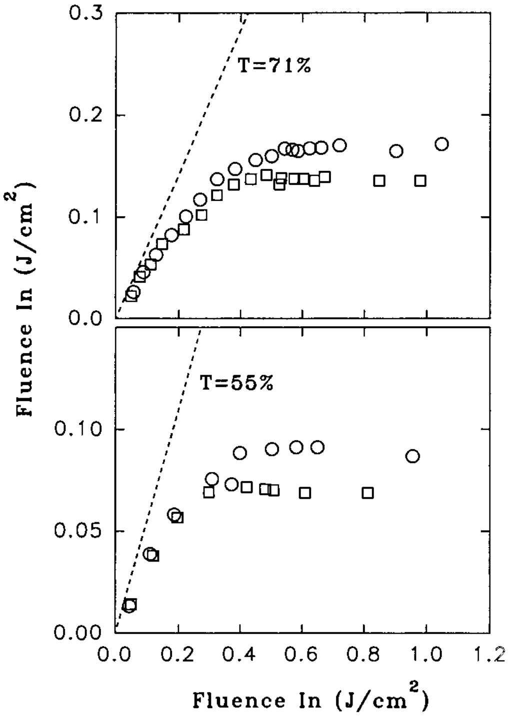

Figure 6. Optical limiting responses of the methano-C_{60} derivative **I** in highly viscous toluene−PMMA polymer blends (○) with 0.25 g/mL PMMA at 71% linear transmittance and 0.4 g/mL at 55% linear transmittance are compared with those in toluene solutions (□) of the same linear transmittances.

viscous toluene−PMMA blends with 0.25−0.4 g/mL of PMMA polymer than in room-temperature solution. For the highly viscous solution of the derivative at 71% linear transmittance, the saturated I_{OUT} value at the optical limiting plateau is ~0.17 J/cm^2, which is ~20% higher than that for the derivative in room-temperature toluene solution of the same linear transmittance (Figure 6a, Table 1). A similar comparison at 55% linear transmittance is shown in Figure 6b. The results suggest that the optical limiting responses of the methano-C_{60} derivative **I** become significantly weaker in the presence of large quantities of PMMA polymer in toluene.

To rule out the possibility of any specific interactions between the methano-C_{60} derivative **I** and PMMA polymer, a highly viscous blend of poly(propionylethyleneimine) (PPEI) polymer in chloroform was also used. The absorption spectrum of the methano-C_{60} derivative **I** in the chloroform−PPEI polymer blend is again essentially the same as that in room-temperature solution (Figure 2). Optical limiting responses of the derivative in the polymer blend containing 0.3 g/mL PPEI polymer ($M_w \approx$ 500 000) were determined in a cuvette of 2 mm optical path length. The result is compared with that of the derivative in room-temperature chloroform solution in Figure 7. At 69% linear transmittance, the saturated I_{OUT} value at the optical limiting plateau is significantly higher for the derivative in the chloroform−PPEI polymer blend than in room-temperature chloroform solution (Figure 7, Table 1). Again, the optical limiting responses of the methano-C_{60} derivative **I** are significantly weaker in the highly viscous solution containing large quantities of high molecular weight PPEI polymer.

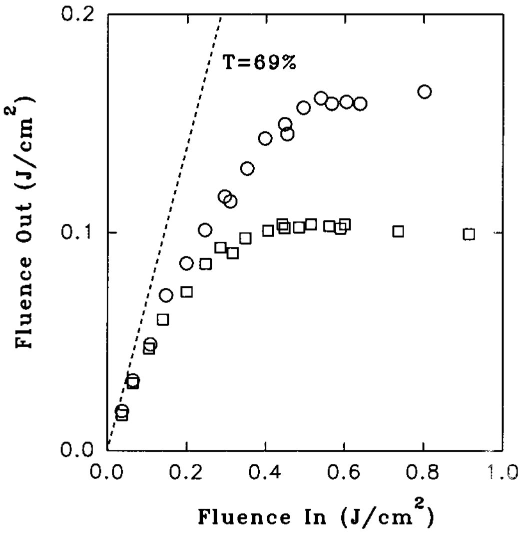

Figure 7. Optical limiting responses of the methano-C_{60} derivative **I** in highly viscous chloroform−PPEI polymer blend with 0.3 g/mL PPEI (○) are compared with those in chloroform solution (□) at a linear transmittance of 69%.

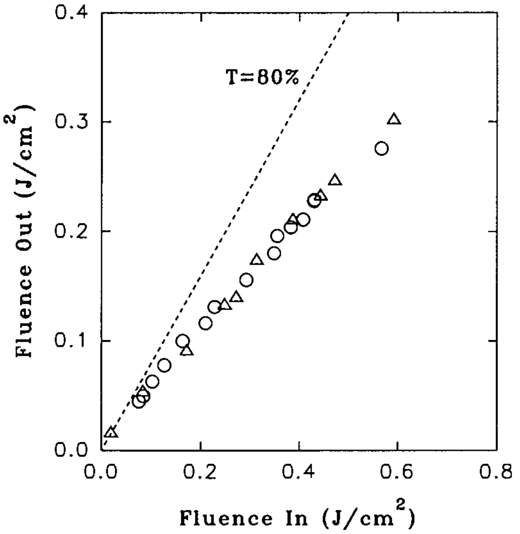

Figure 8. Optical limiting responses of the methano-C_{60} derivative **I** in thin (○) and thick (△) PMMA polymer films of 80% linear transmittance.

Optical Limiting in Polymer Films. Optical limiting properties of the methano-C_{60} derivative **I** in PMMA polymer films were investigated systematically. Thin PMMA films (<0.1 mm) were prepared through spin-casting a highly viscous solution of the derivative in toluene−PMMA polymer blend on a silicon wafer or a glass lantern slide. The thin films thus prepared are optically transparent. The absorption spectrum of the derivative in thin PMMA films is similar to that in room-temperature solution (Figure 2). As a background reference, a blank PMMA polymer thin film was prepared in a similar fashion through spin-casting. The damage threshold of the blank thin film toward nanosecond pulsed laser radiation at 532 nm is higher than 1.2 J/cm^2, consistent with the literature results.[21] However, the thin films containing the methano-C_{60} derivative **I** are more fragile toward the pulsed laser radiation, with a damage threshold of only ~0.6 J/cm^2. Optical limiting responses of the derivative in PMMA polymer thin films were measured. As shown in Figure 8 for the thin film of 80% linear transmittance at 532 nm, the optical limiting responses are much weaker than those of the derivative in room-temperature toluene solution.

Thick PMMA polymer films (0.4 mm) containing the methano-C_{60} derivative **I** have a much improved laser damage threshold. In the film preparation, a concentrated toluene solution of the derivative was mixed with a toluene−PMMA polymer blend to yield a highly viscous reddish-brown solution. The

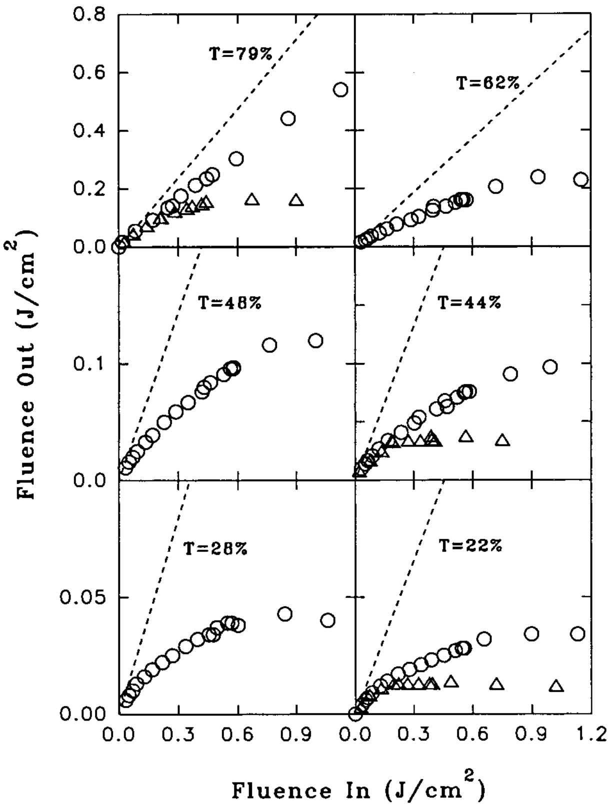

Figure 9. Optical limiting responses of the methano-C_{60} derivative **I** in thick PMMA polymer films (○) are compared with those in toluene solutions of the same linear transmittances (△).

TABLE 2: Optical Limiting Properties of the Methano-C_{60} Derivative I in Thick PMMA Polymer Films (~0.4 mm) and in Toluene Solution

medium	T (532 nm)	I_{OUT} (J/cm^2)^a	T/T_0^{a}
PMMA film	79%	0.50	0.63
toluene	79%	0.16	0.20
PMMA film	62%	0.23	0.37
PMMA film	48%	0.12	0.25
PMMA film	44%	0.10	0.23
toluene	44%	0.04	0.09
PMMA film	27%	0.04	0.15
PMMA film	22%	0.03	0.14
toluene	22%	0.01	0.05
PMMA film	15%	0.02	0.13
PMMA film	9%	0.01	0.11
PMMA film	5%	0.003	0.06

^{a} At I_{IN} = 1 J/cm^2.

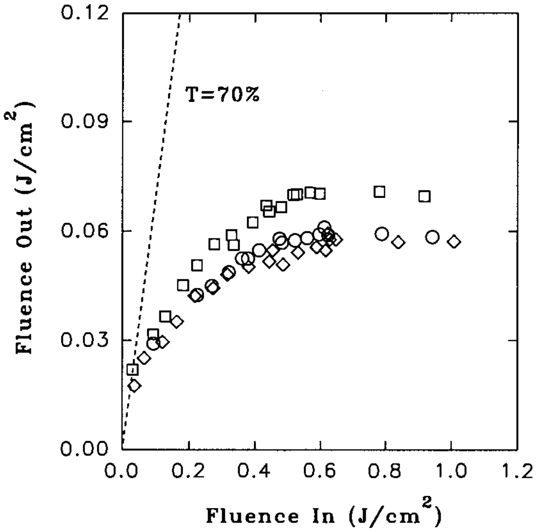

Figure 10. Optical limiting responses of chloroaluminum phthalocyanine **II** in room-temperature DMF solution (□) and DMF−PMMA polymer blends with PMMA contents of 0.1 g/mL (◆) and 0.2 g/mL (○).

highly viscous solution was added to a glass mold uniformly to allow curing in a dust-free environment in the dark for several days to ensure a complete removal of the solvent toluene. A series of fullerene-containing thick PMMA polymer films with different linear transmittances at 532 nm were obtained. To maintain the same film thickness in the series, the highly viscous solutions for curing were prepared such that they all contain the same amounts of PMMA polymer and toluene. The linear transmittance at 532 nm was varied in the series of thick PMMA films by controlling the fullerene concentration in the highly viscous PMMA polymer solutions for curing. The laser damage threshold of the thick films is greater than 1.2 J/cm^2.

The absorption spectrum of the methano-C_{60} derivative **I** in thick PMMA polymer films is essentially the same as that in thin PMMA films and similar to that in room-temperature solution (Figure 2). Shown in Figure 9 are optical limiting results of the thick films with linear transmittances from 22% to 79% at 532 nm. As summarized in Table 2, the optical limiting responses are rather weak at high linear transmittances but become more pronounced in the thick films of lower linear transmittances. For example, the film of 44% linear transmittance has a saturated I_{OUT} value of ~0.1 J/cm^2 at the optical limiting plateau. Also shown in Figure 9 for comparison are optical limiting responses of the derivative in toluene solutions of the same linear transmittances. Obviously, the optical limiting responses are considerably weaker in the thick PMMA polymer films than in the corresponding room-temperature toluene solutions (Table 2). For example, the saturated I_{OUT} value at the optical limiting plateau for the solution of 44% linear transmittance at 532 nm is only ~0.04 J/cm^2.

A comparison of the optical limiting properties of the methano-C_{60} derivative **I** in thin and thick PMMA films of 80% linear transmittance at 532 nm is shown in Figure 8. The result suggests that the optical limiting responses are essentially film thickness independent.

Chloroaluminum Phthalocyanine. Chloroaluminum phthalocyanine **II** is an excellent reverse saturable absorptive optical limiter.[7,8ab] It was used as a reference for optical limiting measurements under the same experimental conditions as those for C_{60} and the methano-C_{60} derivative **I**. A series of solutions of the phthalocyanine **II** in dimethylformamide (DMF) at different concentrations from 2.7×10^{-5} to 2.7×10^{-3} M were used in the measurements. With the use of cuvettes of different optical path lengths, the linear transmittance at 532 nm was kept constant at 70%. As shown in Figure 5c, optical limiting responses of the phthalocyanine **II** are hardly dependent on solution concentrations. The saturated I_{OUT} values at the optical limiting plateau are around 0.06 J/cm^2 for all of the chloroaluminum phthalocyanine solutions (Figure 5c). The result is very different from those of the methano-C_{60} derivative **I** (Figure 5a) and C_{60} (Figure 5b) solutions.

Optical limiting responses of chloroaluminum phthalocyanine **II** in highly viscous DMF−PMMA polymer blends were measured at 70% linear transmittance at 532 nm. The results are compared with those in room-temperature DMF solution of the same linear transmittance in Figure 10. Unlike the methano-C_{60} derivative **I**, the phthalocyanine **II** exhibits similar optical limiting responses in the highly viscous polymer blends and in room-temperature solution at the same linear transmittance (Figure 10). Apparently, the optical limiting properties of chloroaluminum phthalocyanine **II** are essentially unaffected by the presence of large quantities of PMMA polymer in the DMF solution.

Discussion

The optical limiting properties of the methano-C_{60} derivative **I** are quite similar to those of the parent C_{60}. For both fullerene molecules, optical limiting responses in room-temperature solutions are strongly dependent on solution concentrations (Figure 5a,b, Table 1). The results were somewhat surprising in light of the conclusion already in the literature.[16] Thus, experimental artifacts were first suspected. However, the optical limiting results at different solution concentrations are easily reproducible. It is also unlikely that the results of concentration dependence are due to molecular aggregation effects, because not only does the methano-C_{60} derivative **I** have much better solubility characteristics than the parent C_{60} but also some of the concentrations used in the measurements should be considered as very dilute. Of particular significance is the fact that the optical limiting properties of chloroaluminum phthalocyanine **II** measured under the same experimental conditions are clearly concentration independent (Figure 5c). The results for the phthalocyanine **II** are consistent with those already in the literature.[8] The comparative optical limiting experiments for the fullerenes and chloroaluminum phthalocyanine **II** show that the observed strong concentration dependence of optical limiting for the fullerenes cannot be due to the experimental setup or any optical artifacts. In fact, the conclusion in the literature[16] that the clamped level of the output fluence at the optical limiting plateau is determined by the amount of C_{60} in the beam path was based on optical limiting measurements at solution concentrations over a relatively narrow range (1×10^{-4} to 4×10^{-4} M). According to Figure 5b, the changes in optical limiting responses of C_{60} over such a narrow concentration range are relatively small so that the concentration dependence of optical limiting is not so obvious. In the present study, however, the concentrations of C_{60} and the methano-C_{60} derivative **I** are varied over 2 orders of magnitude, which makes it easier to detect the strong concentration dependence. The inclusion of more dilute solutions (1.23×10^{-5} o 6.16×10^{-5} M) in the measurements is particularly important because the optical limiting responses of the fullerenes change significantly over the concentration range (Figure 5a,b, Table 1).

An interesting observation is that the concentration dependence of optical limiting disappears at very low fullerene concentrations. For the methano-C_{60} derivative **I**, the optical limiting responses become significantly weaker when the solution concentration is reduced from 6.16×10^{-5} (20 mm optical path length) to 2.46×10^{-5} M (50 mm optical path length) but remain essentially the same when the solution concentration is reduced further by a factor of 2 from 2.46×10^{-5} to 1.23×10^{-5} M (Figure 5a, Table 1). Thus, the threshold concentration for the concentration dependence of optical limiting is in the 2.46×10^{-5} to 6.16×10^{-5} M range for the methano-C_{60} derivative **I** in room-temperature toluene. Mechanistically, the concentration dependence is likely a reflection of optical limiting contributions associated with bimolecular excited-state processes, which are in addition to the unimolecular reverse saturable absorptive optical limiting contributions described by the five-level model in Figure 1. The threshold represents the minimum fullerene solution concentration required for the bimolecular excited-state processes to be significant with respect to optical limiting toward nanosecond laser pulses.

In the absence of contributions from any bimolecular excited-state processes, the optical limiting responses of fullerenes are often modeled in terms of the five-level reverse saturable absorption scheme shown in Figure 1.[9] The fundamental differential equation for the scheme is written as follows.

$$\mathrm{d}i/\mathrm{d}x = -i(\sigma_G N_G + \sigma_S N_S + \sigma_T N_T) \tag{1}$$

where i represents the photon flux (photons cm^{-2} s^{-1}) as it changes with distance x through the sample of a path length L, σ denotes absorption cross sections (cm^2) of the electronic states shown in Figure 1, and N represents the molecular populations in the different states. Under the assumption of negligible populations in the upper excited states, the changes in the state populations with time are typically described as follows:[9]

$$\mathrm{d}N_S/\mathrm{d}t = \sigma_G N_G i - (k_{SG} + k_{ISC})N_S \tag{2}$$

$$\mathrm{d}N_T/\mathrm{d}t = k_{ISC}N_S - k_{TG}N_T \tag{3}$$

An expression for N_G is not necessary because of the relationship $N_G = N_0 - (N_S + N_T)$, where N_0 is the total molecular population. The condition for reverse saturable absorption is that the excited-state cross sections are larger than the ground-state cross section, $\sigma_{EFF}/\sigma_G > 1$, where σ_{EFF} is a weighted average of σ_S and σ_T.[6] For C_{60}, both σ_S and σ_T are larger than σ_G at 532 nm.[9,26] Thus, the optical limiting of C_{60} definitely consists of contributions from the reverse saturable absorption as a result of $\sigma_{EFF}/\sigma_G > 1$. In fact, since the intersystem crossing yield of C_{60} is unity, the reverse saturable absorptive optical limiting responses toward 5−10 ns laser pulses are due predominantly to the large triplet−triplet absorption cross section, namely $\sigma_T/\sigma_G > 1$. This was confirmed in the correlation of the optical limiting results of C_{60} in room-temperature toluene with the five-level reverse saturable absorption model (Figure 1) by numerically solving eqs 1−3.[9] Despite the successful correlation, however, the model in Figure 1 consists of only unimolecular excited-state processes, with no processes that are dependent on fullerene concentrations. Thus, it obviously cannot account for the large variations in the optical limiting response with changes in the C_{60} solution concentration (Figure 5b, Table 1).

The optical limiting behavior of the methano-C_{60} derivative **I** may be similarly considered in the same mechanistic framework. The intersystem crossing yield of the derivative is also unity, according to the result of photosensitization for singlet molecular oxygen generation.[28,29] There is also the ratio $\sigma_T/\sigma_G > 1$ for the derivative, suggesting optical limiting contributions from the unimolecular reverse saturable absorption mechanism shown in Figure 1. More quantitatively, however, the ground-state absorption cross section of the derivative is larger than that of C_{60} (4.78×10^{-18} cm^2 vs 3.59×10^{-18} cm^2 at 532 nm) and the triplet−triplet absorption cross section of the derivative is smaller than that of C_{60} at 532 nm (Figure 3). Thus, $(\sigma_T/\sigma_G)_{\mathrm{DERIVATIVE}} < (\sigma_T/\sigma_G)_{C60}$, which would suggest weaker optical limiting responses for the derivative in the context of the unimolecular five-level reverse saturable absorption model (Figure 1). The experimental results show otherwise. The optical limiting responses of the methano-C_{60} derivative **I** in a room-temperature toluene solution of 6.16×10^{-4} M concentration (2 mm optical path length and 70% linear transmittance) are not so different from those of C_{60} obtained under similar conditions (Figure 4, inset). The discrepancy between the model prediction and experimental results suggests that the optical limiting results of C_{60} and the methano-C_{60} derivative **I** can hardly be accounted for quantitatively using the unimolecular five-level reverse saturable absorption model (Figure 1). A more likely scenario is that for the fullerenes in solution at the concentrations commonly used for optical limiting measurements, the observed optical limiting responses are dominated by the contributions associated with bimolecular excited-state processes. The similarity in the optical limiting results of C_{60} and the derivative in relatively concentrated solutions is probably a reflection of the similarity in their bimolecular excited-state processes. With respect to contributions from the unimolecular reverse saturable absorption mechanism (Figure 1), the difference between C_{60} and the methano-C_{60} derivative **I** (as related to the fact that $(\sigma_{\mathrm{T}}/\sigma_{\mathrm{G}})_{\mathrm{DERIVATIVE}} < (\sigma_{\mathrm{T}}/\sigma_{\mathrm{G}})_{\mathrm{C60}}$) can be observed at solution concentrations below the threshold for the concentration dependence of optical limiting. For example, at the fullerene solution concentrations corresponding to a 50 mm optical path length for 70% linear transmittance, the optical limiting responses of the derivative are noticeably weaker than those of C_{60} (Figure 5a,b), with I_{OUT} values of 0.3 J/cm^2 for the derivative vs 0.235 J/cm^2 for C_{60} at $I_{\mathrm{IN}} = 1$ J/cm^2.

It is most likely that the optical limiting properties of the fullerenes in solution at concentrations above the threshold for concentration dependence are significantly affected by bimolecular excited-state processes. The bimolecular processes can in principle be associated with both the excited singlet and triplet states of the fullerenes. According to results from time-resolved fluorescence investigations,[25,30] the fluorescence lifetimes of C_{60} and the methano-C_{60} derivative **I** in room-temperature solution are concentration independent over the concentration range under consideration. It may be concluded that the excited singlet-state decays of the fullerenes in solution, which are dominated by the efficient intersystem crossing to the formation of excited triplet state, are independent of changes in the fullerene solution concentration. Thus, the observed strong concentration dependence of optical limiting (Figure 5a,b) must be due to excited triplet-state bimolecular processes of the fullerenes. In fact, concentration effects on the excited triplet-state properties of fullerenes are well documented.[31,32] In a series of careful flash photolysis experiments, Weisman and co-workers have shown that the excited triplet state decays and lifetimes of C_{60} and methano-C_{60} derivatives in room-temperature solution are strongly dependent on fullerene concentrations.[31,32] The strong concentration dependence is attributed to bimolecular processes including the self-quenching of the fullerene excited triplet state by ground-state fullerene molecules and triplet−triplet annihilation.[31,32] In principle, these bimolecular processes may contribute to the observed optical limiting responses of fullerenes toward 5−10 ns laser pulses in at least two possible ways. One is the direct formation of a triplet excimer-like state[33] with a large absorption cross section.

$$^3C_{60}^* + C_{60} \rightarrow {}^3(C_{60}C_{60})^* \tag{4}$$

The other is due to triplet−triplet annihilation.[33,34]

$$^3C_{60}^* + {}^3C_{60}^* \begin{cases} \xrightarrow{(1/9)k_{\mathrm{TT}}} {}^1(C_{60}C_{60})^{**} & \text{(5a)} \\ \xrightarrow{(3/9)k_{\mathrm{TT}}} {}^3(C_{60}C_{60})^{**} & \text{(5b)} \\ \overset{(5/9)k_{\mathrm{TT}}}{\rightleftharpoons} {}^5(C_{60}C_{60})^{**} & \text{(5c)} \end{cases}$$

where the double asterisks denote doubly excited pairs and K_{TT} is the triplet−triplet annihilation rate constant. The singlet and triplet doubly excited pairs formed initially from the triplet−triplet annihilation rapidly relax to singlet and triplet excimer-like states.[34]

$$^1(C_{60}C_{60})^{**} \rightarrow {}^1(C_{60}C_{60})^* \tag{6a}$$

$$^3(C_{60}C_{60})^{**} \rightarrow {}^3(C_{60}C_{60})^* \tag{6b}$$

On a longer time scale, other absorbing states may be formed from the initial excited-state species generated in the triplet−triplet annihilation process.

The possible contributions from these excited-state bimolecular processes may still be discussed within the framework of nonlinear absorptions due to the excited-state absorption cross sections being larger than the ground-state absorption cross section. The unimolecular five-level reverse saturable absorption model shown in Figure 1 may therefore be modified to include the bimolecular excited-state processes. In principle, all of the absorbing species including the doubly excited pairs (eq 5) should be considered in the mechanistic model. In practice, however, a simplified treatment may be justified. Under the assumption that the optical limiting properties of fullerenes are significantly affected by absorptions of the singlet and triplet excimer-like states, the modified reverse saturable absorption model for fullerenes that includes both unimolecular and bimolecular excited-state processes is shown in Figure 11. The corresponding differential equations for the modified model may be written as follows.

$$\mathrm{d}i/\mathrm{d}x = -i(\sigma_{\mathrm{G}}N_{\mathrm{G}} + \sigma_{\mathrm{S}}N_{\mathrm{S}} + \sigma_{\mathrm{T}}N_{\mathrm{T}} + \sigma_{\mathrm{S_{ex}}}N_{\mathrm{S_{ex}}} + \sigma_{\mathrm{T_{ex}}}N_{\mathrm{T_{ex}}}) \tag{7}$$

$$\mathrm{d}N_{\mathrm{S}}/\mathrm{d}t = \sigma_{\mathrm{G}}N_{\mathrm{G}}i - (k_{\mathrm{SG}} + k_{\mathrm{ISC}})N_{\mathrm{S}} \tag{8}$$

$$\mathrm{d}N_{\mathrm{T}}/\mathrm{d}t = k_{\mathrm{ISC}}N_{\mathrm{S}} - k_{\mathrm{TG}}N_{\mathrm{T}} - (4/9)k_{\mathrm{TT}}N_{\mathrm{T}}2 - k_{\mathrm{T_{ex}}}N_{\mathrm{T}}N_{\mathrm{G}} \tag{9}$$

$$\mathrm{d}N_{\mathrm{S_{ex}}}/\mathrm{d}t = (1/9)k_{\mathrm{TT}}N_{\mathrm{T}}2 - k_{\mathrm{S_{ex}D}}N_{\mathrm{S_{ex}}} \tag{10}$$

$$\mathrm{d}N_{\mathrm{T_{ex}}}/\mathrm{d}t = k_{\mathrm{T_{ex}}}N_{\mathrm{T}}N_{\mathrm{G}} + (3/9)k_{\mathrm{TT}}N_{\mathrm{T}}2 - k_{\mathrm{T_{ex}D}}N_{\mathrm{T_{ex}}} \tag{11}$$

where the subscripts S_{ex} and T_{ex} denote singlet and triplet eximer-like states, respectively.

Experimentally, significant self-quenching of C_{60} excited triplet state by ground-state C_{60} molecules has been observed at moderate solution concentrations, but triplet excimer of C_{60} has not been detected. However, the results from laser flash photolysis measurements are not sufficient to rule out the possibility of an excimer-like state on the time scale of a few nanoseconds. Short-lived complexes of ground and excited triplet-state fullerene molecules that are strongly absorptive may be populated directly under the intense pulsed laser irradiation or through the triplet−triplet annihilation process, contributing to the optical limiting of fullerenes in solution.

For the triplet−triplet annihilation in fullerene solution, while there has been no report of any delayed singlet transient absorption from the bimolecular process, its strong effect on the excited triplet-state decay of fullerenes in laser flash photolysis experiments is well documented.[31,32] Under the condition of high laser power densities in optical limiting measurements, which is much different from that in transient absorption experiments, the triplet−triplet annihilation process is likely more significant. In addition to the light intensity, the triplet−triplet annihilation depends on the concentration of ground-state fullerene molecules. At a constant linear transmittance in optical limiting measurements, lower solution concentration corresponds to longer optical path length, which makes

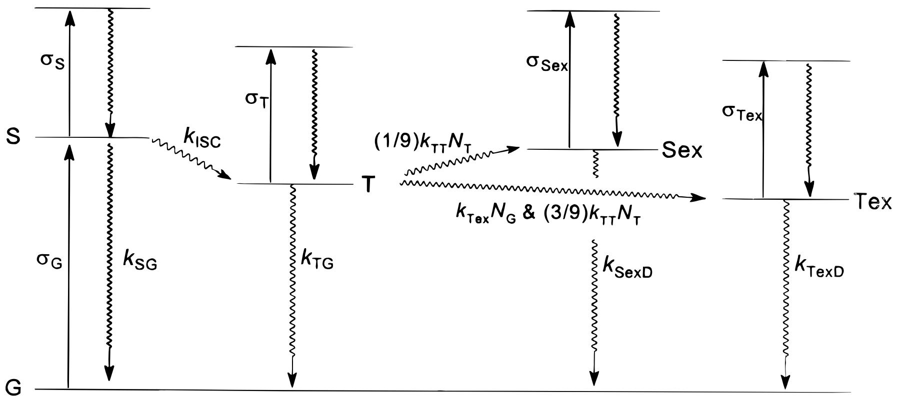

Figure 11. Proposed reverse saturable absorption mechanism for fullerenes that includes both unimolecular and bimolecular excited-state processes.

it less likely to generate a high local concentration of excited triplet fullerene molecules in the laser beam path for efficient triplet−triplet annihilation.

Optical limiting contributions that are associated with excited triplet-state bimolecular processes such as self-quenching and triplet−triplet annihilation might be unique to the fullerenes. The same concentration-dependent effects are absent in the optical limiting of metallophthalocyanine in solution (Figure 5c). It is probably more than a coincidence that the fullerene excited triplet-state decays are also affected by bimolecular processes in an unusually efficient fashion.[31,32]

The excited-state bimolecular processes are diffusional or pseudodiffusional processes. The pseudodiffusional processes are those in which the involved molecules are in close proximity due to high local concentrations. These molecular diffusion-dependent processes are hindered significantly in highly viscous media. For the methano-C_{60} derivative **I** in nonreactive solvent−polymer blends, toluene−PMMA and chloroform−PPEI, the observed optical limiting responses are weaker than those in room-temperature solution (Figures 6 and 7, Table 1). The results are apparently not polymer specific. Since PMMA and PPEI polymers have very different structures and chemical properties, the effects on the fullerene optical limiting performance must be associated with their physical properties. A common physical characteristics of the solvent−polymer blends is the high viscosity, which hinders diffusion-dependent processes. Thus, the weaker optical limiting responses of the methano-C_{60} derivative **I** in the highly viscous solvent−polymer blends may be attributed to less optical limiting contributions from the nonlinear absorptions that are associated with the excited triplet-state bimolecular processes (Figure 11).

Evidently, the optical limiting properties of fullerenes are dependent on both the solution concentration and viscosity. Both dependencies may be consistently accounted for within the framework of the reverse saturable absorption mechanism that includes both unimolecular and bimolecular processes (Figure 11). The viscosity effect is included in the mechanism as a parameter in rate constants for the bimolecular excited-state processes (k_{TT} and $k_{T_{ex}}$, eqs 8−11).

For fullerenes in polymer films and solid-state matrixes, diffusional or pseudodiffusional processes on the nanosecond time scale become essentially impossible. The absence of any optical limiting contributions that are associated with excited triplet-state bimolecular processes (Figure 11) is likely responsible for the much weaker optical limiting responses of C_{60} and the methano-C_{60} derivative **I** in PMMA films (Figures 8 and 9). In fact, the optical limiting results in the polymer films probably reflect the true unimolecular reverse saturable absorption behavior of the fullerenes, which may be modeled by the simple five-level mechanism shown in Figure 1. Without the contributions associated with the excited triplet-state bimolecular processes, the optical limiting responses of the fullerenes in PMMA films are dependent only on linear transmittances of the films (namely the number of molecules in the laser beam path) but independent of the optical path length (namely the film thickness). This is confirmed by the results shown in Figure 8. The optical limiting responses of the methano-C_{60} derivative **I** in thin (<0.1 mm) and thick (~0.4 mm) PMMA films of the same linear transmittance are indistinguishable, despite the fact that the film thicknesses (or the optical path lengths) differ by more than a factor of 4.

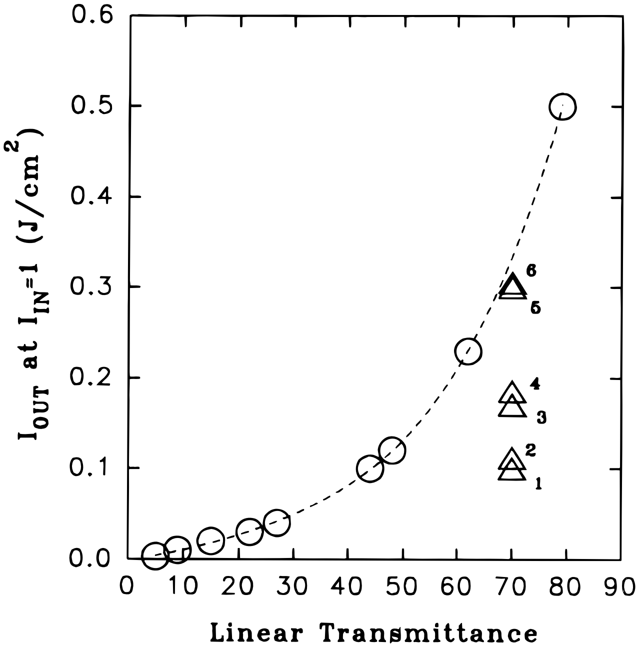

Figure 12. Optical limiting results of the methano-C_{60} derivative **I** in toluene solutions (△) of different concentrations (1) 1.23×10^{-3} M; (2) 6.16×10^{-4} M; (3) 1.23×10^{-4} M; (4) 6.16×10^{-5} M; (5) 2.46×10^{-5} M; and (6) 1.23×10^{-5} M) and in thick PMMA polymer films (○) of different linear transmittances. The output fluences at the input fluence of 1 J/cm^2 are plotted as a function of the sample linear transmittance.

Optical limiting properties of the fullerenes in room-temperature solution and in polymer films can be explained consistently in terms of the mechanistic model shown in Figure 11. The results shown in Figure 12 serve as more quantitative evidence for such a conclusion. For the methano-C_{60} derivative **I** in a series of thick PMMA films of varying linear transmittances, the output fluences at the constant input fluence of 1 J/cm^2 ($I_{OUT,IN=1}$) are different, decreasing monotonically with decreasing linear transmittance of the films. The relationship between $I_{\mathrm{OUT,IN=1}}$ and the linear transmittance is well represented by a smooth curve (Figure 12). On the other hand, for the derivative in toluene solutions of a constant linear transmittance of 70%, the optical limiting responses are solution concentration dependent, with $I_{\mathrm{OUT,IN=1}}$ increasing steadily with decreasing solution concentration (Figure 12). The data points corresponding to the low solution concentrations of 1.23×10^{-5} and 2.46×10^{-5} M, which are below the threshold for concentration dependence of optical limiting, fall right on the smooth curve for the optical limiting results of the derivative in PMMA polymer films (Figure 12). The results again suggest that the optical limiting behavior of the methano-C_{60} derivative **I** in PMMA polymer films is close to that in room-temperature solution in the absence of effects associated with the concentration-dependent bimolecular excited-state processes. The excited triplet-state bimolecular processes in the mechanistic model shown in Figure 11 are absent for fullerenes in polymer films due to the lack of molecular diffusion and in dilute solutions because the concentrations are too low to support meaningful bimolecular processes on the excited-state time scale. Under such conditions, the mechanistic model shown in Figure 11 becomes equivalent to the simple five-level reverse saturable absorption model shown in Figure 1.

In addition to PMMA polymer films, other solid-state matrixes such as sol−gel glasses also have significant effects on the optical limiting performance of fullerenes, resulting in substantially weaker optical limiting responses.[17−20] Mechanistic explanations including a change in nonlinear scattering from solution to solid-state matrix[18,19] and thermal effects[20] have been proposed. While there may be contributions to the optical limiting of fullerenes from these mechanisms in addition to nonlinear absorptions, especially at high input fluences, the contributions are likely insignificant compared to the effects that are associated with the bimolecular excited-state processes discussed above. For chloroaluminum phthalocyanine **II** in room-temperature solution, the optical limiting responses are solution concentration independent (Figure 5c). It is no coincidence that there are also no medium viscosity effects and that the optical limiting results of the molecule in solution and in solid-state matrixes are the same.[35]

Summary

The optical limiting properties of C_{60} and the methano-C_{60} derivative **I** are both strongly dependent on solution concentrations above a threshold concentration, which is in the range of 2.46×10^{-5} to 6.16×10^{-5} M for the derivative. The medium viscosity also has great effects on the optical limiting performance of the fullerenes, resulting in weaker optical limiting responses for the fullerenes in highly viscous solvent−polymer blends. The lack of meaningful molecular diffusion in polymer films is likely the cause for the much poorer optical limiting performance of the fullerenes in both thin and thick PMMA films than in room-temperature solution. The optical limiting responses of the methano-C_{60} derivative **I** in PMMA polymer films are independent of the concentration in the laser beam path, indicating a different behavior from that of the derivative in room-temperature solution.

Both the solution concentration dependence and medium viscosity dependence are attributed to effects on optical limiting contributions that are associated with excited triplet-state bimolecular processes, in particular self-quenching and triplet−triplet annihilation. The fullerene solution concentration affects the efficiency of the bimolecular excited-state processes directly, while the medium viscosity affects the bimolecular rate constants through changes in the molecular diffusivity. In fact, the optical limiting responses of the methano-C_{60} derivative **I** in room-temperature toluene solution at very low concentrations, which are below the threshold for concentration dependence of optical limiting, are similar to those of the derivative in PMMA polymer films. The results show, for the first time, that the optical limiting results of fullerenes in solution and in polymer films can be consistently accounted for in a single mechanistic framework. A modified reverse saturable absorption model that includes both unimolecular and bimolecular excited-state processes is proposed for the optical limiting properties of fullerenes. Further investigations using fast kinetic techniques to detect experimentally the bimolecular processes and to determine the related parameters are needed for a quantitative modeling of the fullerene optical limiting properties.

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