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Optical limiting and nonlinear optical absorption properties of C_{60}–polystyrene star polymer films: C_{60} concentration dependence

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The optical limiting behavior and the nonlinear optical properties of pure C_{60}–(polystyrene$_x$)$_y$ (C_{60}–(PS$_x$)$_y$) star polymer, and C_{60}–(PS$_x$)$_y$ incorporated in a polystyrene matrix, are reported. Two, four and six polystyrene arms of controllable length were grafted directly on the C_{60} cage, preventing aggregation of the fullerene molecule, and consequently permitting achievement of high C_{60} concentrations. The optical limiting behavior of these films was measured below the damage threshold, and the nonlinear absorption coefficient β was determined by the Z-scan technique, using nanosecond 532 nm and sub-picosecond 497 nm laser radiation. In some of the samples, the high concentration of C_{60} gives rise to intermolecular interactions, which diminish the average molecular nonlinear optical properties of the film. However, the observed dependence of the nonlinear optical properties as a function of laser pulse duration and C_{60} concentration may be relevant to applications of these compounds in solid state devices.

Introduction

C_{60}, higher fullerenes and fullerene derivatives have attracted a lot of research effort this last decade for their potential applications.[1–9] In particular, the large number of conjugated π bonds and their symmetrical arrangement within the fullerene cage contribute to a large and fast nonlinear optical response and suggest numerous applications in optical data processing,[8] all optical switching[9] for optical communications, eye and optical detector protection,[1] *etc.* This last asset has led to numerous studies on the relevant parameters and properties of optical limiting (OL) of C_{60} and other fullerenes.[1,2,9–13]

However, due to their electrophilic properties and because of strong intermolecular interactions, fullerenes are in general sparingly soluble in most organic solvents, and they tend to aggregate. It has been shown that the triplet state quantum yield decreases as a result of either dimerisation and/or aggregation of the C_{60} molecule.[14,15] This usually shortens the excited state lifetime,[16] altering the optical properties of the molecule. In addition, under sub-picosecond laser excitation, where nonlinear absorption through a long lived triplet state cannot occur, aggregation and intermolecular interactions could also modify the geometry of the delocalized π-electron clouds and therefore reduce the electronic nonlinear optical response. In view of these facts and in order to be able to increase the concentration of fullerene without aggregation, several approaches of either molecular engineering and grafting,[17–22] or embedding the fullerene cages in various matrices,[23–28] have been proposed. Among others, one approach recently proposed is based on the addition of various "living" anionic polymers on C_{60},[29] producing star-like polymer structures[18] where a given number of polymer arms are branched off a fullerene cage.[30–32] This synthesis technique offers the possibility of preparing 3D architectures that would allow one to control the effective C_{60} concentration over wider ranges, by preventing close contact between fullerene cages even at concentrations significantly above the threshold of pure C_{60} aggregation in organic solvents (*e.g.* 3.4 mM for toluene[33]).

The nonlinear optical properties of C_{60}–(PS$_x$)$_6$ star polymers in solution have been recently studied.[34,35] In this work, we investigate the nonlinear optical properties of solid-state films of C_{60}–(PS$_x$)$_y$ star polymers having two, four or six identical polystyrene arms of variable molecular weight grafted onto the C_{60} cage.

Experimental

The compounds were prepared by grafting anion polystyrene chains (PS^- Li^+) on to a C_{60} cage in toluene where the polystyrene anion was added onto a double bond of the fullerene.[36] Since the polydispersity is very low using this technique, the number of grafted chains and the length of the arm could be easily controlled. The method allowed grafting of up to six PS arms on to the C_{60} cage, where the arms are of almost equal length, resulting in star-shaped molecular structures.[18] The photophysical properties of the six-arm C_{60}–polystyrene star C_{60}–(PS$_{1400}$)$_6$ in solution have been reported recently.[37] The quantum yield for the production of the triplet state was found to be lower (0.65) than that of the C_{60} molecule in toluene solution (∼1).[37] The reduction of the triplet state quantum yield with respect to C_{60} in solution can be understood in terms of the loss of double bonds of the C_{60} cage after grafting of the PS chains[17] and because of the solid state nature of the films studied here. Furthermore, triplet–triplet absorption spectra showed a peak near 650 nm, blue shifted by about 100 nm as compared to C_{60},[13] a shift similar to

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Table 1 Chemical composition and C_{60} reduced concentration of the studied films and of the C_{60} and C_{60}–$(PS_x)_y$ solutions used for comparison

				Composition (%)			
Sample	No. of arms	Thickness/μm	MW of PS arm	C_{60}–PS_x	Unlinked PS	Added PS_{230000}	$[C_{60}]$/mM
SF1	6	80	90 000	68	32	0	2.35
SF2	6	140	90 000	81	19	0	2.68
SF3	6	200	90 000	86.5	13.5	0	2.81
SF4	6	150	3380	44.6	9.6	45.8	37.89
SF5	6	160	16 550	34.5	20	45.5	6.56
SF6	6	390	9000	51.8	0	48.2	17.12
SF7	6	100	200 000	19.65	0	80.34	0.42
SF8	6	110	200 000	100	0	0	1.97
SF9	2	80	45 000	24.3	0	75.7	9.36
SF10	4	90	90 000	46.4	0	53.6	3.80
S	6	1000	4800	100	0	0	1.00
C_{60}	0	1000	0	0	0	0	3.70

that reported for other fullerene compounds with addends.[15,38] Finally, the lifetime of the lowest triplet state of the hexa-adduct was found to be less than 50 μs.

Free-standing C_{60}–$(PS_x)_6$ films were prepared from a toluene solution of either a mixture of C_{60}–$(PS_x)_6$ with PS_{230000} or pure C_{60}–$(PS_x)_y$ (10–15 mg ml^{-1}). The solutions were stirred for several hours to ensure total dissolution and filtered through a 0.45 μm polypropylene filter before use. The film casting took place on a clean mercury surface under a flow of nitrogen. Small quantities of solution were repeatedly deposited in the center of a Teflon ring floating on the mercury and submitted to slow evaporation. After complete evaporation, the films were dried under vacuum. Unlinked $(PS)_x$ arms remained in the solution and are present in some of the films. When the MW of the PS arm was small (*i.e.* less than ~30 000), at least 10 mol% of PS_{230000} was added in order to plasticize the film and strengthen its cohesion. The samples were shaped as small disks of either 1 or 2 cm diameter surrounded by a ring holder. A transmission variation in the range of 5% was observed, attributed to local thickness variations or to local C_{60} concentration changes. For all samples, a reduced concentration of C_{60} was calculated from the % weight employed for the synthesis of the films. Table 1 summarizes the composition and the thickness of ten different films studied here. UV–Visible–NIR absorption spectra of the films were measured by means of a Varian Cary 50 spectrophotometer with a resolution of 1.5 nm.

The triplet–triplet absorption of the films was measured using a standard transient absorption setup equipped with a Quantel Nd : YAG laser (532 nm, 6 ns pulses at a frequency of 10 Hz). The laser pulse energy was measured in mJ by a laser monitor model 900, Laser Instruments Ltd. In addition, fluorescence measurements were carried out by the single photon counting method with laser excitation at 595 nm from a Spectra Physics rhodamine 6G dye laser model 375 synchronously pumped by a Spectra Physics model 2030, 82 MHz mode locked argon ion laser as previously described.[39]

The measurements of the nonlinear optical parameters were performed employing two different laser radiation sources: a 10 ns, 532 nm frequency-doubled Spectron Nd : YAG laser and a 0.5 ps, 496 nm DFDL (Distributed Feedback Dye Laser) laser system. We measured the transmission variation of the sample for various positions along the focal plane (Z-scan method[40]) in order to determine the nonlinear absorption coefficient β of the films. However, prior to these measurements and because of the low damage threshold of the polystyrene moiety of the fullerene–polystyrene films, we checked the transmission of each sample for various fluences (energy cm^{-2}) under constant focusing conditions. This allowed us to determine the optical limiting action of the films and any damage threshold present. Special care was taken in each case to ensure that the Z-scan experiments were performed below this threshold. The laser beam was focused with a 150 mm focal length lens resulting in a beam waist of around 130 μm for both laser sources. Two Glan polarizers were used to vary laser light input energy and both lasers were operated at repetition rates of a few Hz, in order to avoid thermal effects on the samples surface. For the Z-scan setup, the experimental device and procedure are described in detail elsewhere.[10] In order to avoid destruction of the sample at the beam waist, low input energy was used, the peak intensity being 5 MW cm^{-2} and 150 GW cm^{-2} for the ns and ps sources, respectively. In addition to the samples listed in Table 1, two pure polystyrene samples, with MW 120 000 and 230 000 respectively, were used as standards in order to clarify the role of the PS arms and of unlinked PS chains in optical nonlinearities and in physical processes observed. Optical limiting and Z-scan measurements were each carried out under the same input laser fluence in order to avoid different population redistribution and/or excitation of different nonlinear optical processes in the C_{60} molecule, since under our experimental conditions β can be an effective parameter depending on the incident intensity.[10,41,42] Finally, all samples were examined before and after irradiation by means of an optical microscope to ensure that no surface damage had occurred.

Results

The absorption spectra of some of the films studied and of a pure PS_{120000} film are shown in Fig. 1. All the films, except sample SF9, presented similar visible absorption spectra. The

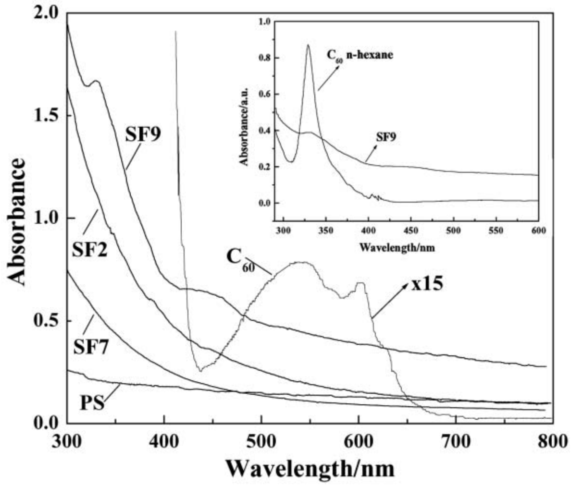

Fig. 1 UV–visible absorption spectra of various films studied. For comparison, the absorption spectrum of C_{60}–hexane solution is also shown. Inset: A close comparison of the spectra of sample SF9 and C_{60}–hexane solution.

spectra exhibited a featureless monotonic decrease from the UV wavelengths to the red wavelengths losing all the fine structure features of the well-known C_{60} spectrum. Several other groups have also observed similar spectra for various fullerene–polymer macromolecules.[43,44] Usually this broadening is considered to result from interactions of the C_{60} moiety with the disordered matrix,[25,26] or to the reduction of the high symmetry of the delocalized π electron cloud of the C_{60} cage, which can be modified by the addition of a donor radical. In addition, the superposition of different absorption spectra due to a high number of different isomeric forms, could also give rise to absorption band broadening, and possibly to a featureless spectrum. Nevertheless, one sample (SF9), which is a bis-adduct C_{60}–$(PS_{45000})_2$, presents a band near 330 nm, which is assigned to the 3 $^1T_{1u}$–1 ^1A_g transition[12] of C_{60}. A comparison of the spectra around 330 nm of film SF9 and C_{60}–*n*-hexane is shown in the inset of Fig. 1. This absorption peak is known to be sensitive to the loss of conjugation and weakens upon chemical modification of the molecular structure of the C_{60} cage.[45,46] This remaining feature is also characteristic of a 1,4-disubstituted C_{60} spectrum and might be taken as evidence of lack of clustering.[26] Due to the lack of clustering in sample SF9, the C_{60} triplet state can be populated more significantly than in the other films, so that it could play a more efficient role in optical limiting in this case.[38]

For a better understanding of the nonlinear optical response of the films studied, their photophysical properties such as the triplet–triplet absorption, the triplet lifetime and fluorescence lifetime were also investigated. Preliminary results of these studies have revealed that the triplet state absorption of a C_{60}–$(PS_{9000})_6$ film exhibits a maximum at 670 nm and its lifetime was found to be less than 10 μs (a value significantly lower than that determined for a C_{60}–benzene solution where oxygen has been removed through bubbling with N_2 (70 μs[37])). This result shows that triplet states are actually produced in films and the reduced value of the lifetime of the triplet state indicates that it is partially quenched probably due either to the presence of oxygen (trapped in the film or diffused through the film after its preparation) and/or to triplet–triplet annihilation.

In order to test this hypothesis, we measured the fluorescence lifetime of the film. The lifetime was found to be about 2.7 ns, a value close to that measured for a solution of the monomer in toluene ($\sim$3.7 ns). This is evidence that the quantum yield of the intersystem crossing resulting in the population of the triplet state is not strongly influenced for the films under study compared with the respective monomer solutions. Therefore, taking into account the above experimental evidence, it seems that the differences between films and monomer solutions are due more to the oxygen quenching effect on the triplet state lifetime than to a possible small matrix effect of quenching of the triplet by triplet–triplet annihilation, which however cannot be ruled out as the singlet lifetime is shortened from 3.7 to 2.7 ns.

As was shown in a previous study[34] of C_{60}–$(PS_x)_y$ (with PS_x of MW varying from 900 to 20500 and y being 3 to 6) diluted in toluene, neither the number of grafted PS arms nor their length played any determining role on the nonlinear absorption properties of the macromolecular system at least for the pulse durations (10 ns and 0.5 ps) and the wavelengths used (532 nm and 496 nm). Furthermore, a comparative study with a pure C_{60}–toluene solution revealed an enhanced nonlinear absorption coefficient β for the C_{60}–$(PS_x)_y$ compound, being 3 to 4 times larger than that of a C_{60}–toluene solution at similar C_{60} concentration. In contrast to these observations, when 100 fs pulses at 800 nm were employed in an optical Kerr effect configuration,[35] the determined third order nonlinearity of the C_{60}–$(PS_x)_y$ compound was found to be more than two orders of magnitude larger than that of C_{60}. In addition, an influence of the number and the length of the arms on the nonlinearity was observed. As reported in this case, the nonlinearity increases with the number of arms and for stars having the same arm number, the nonlinearity is stronger for arms with smaller MW.

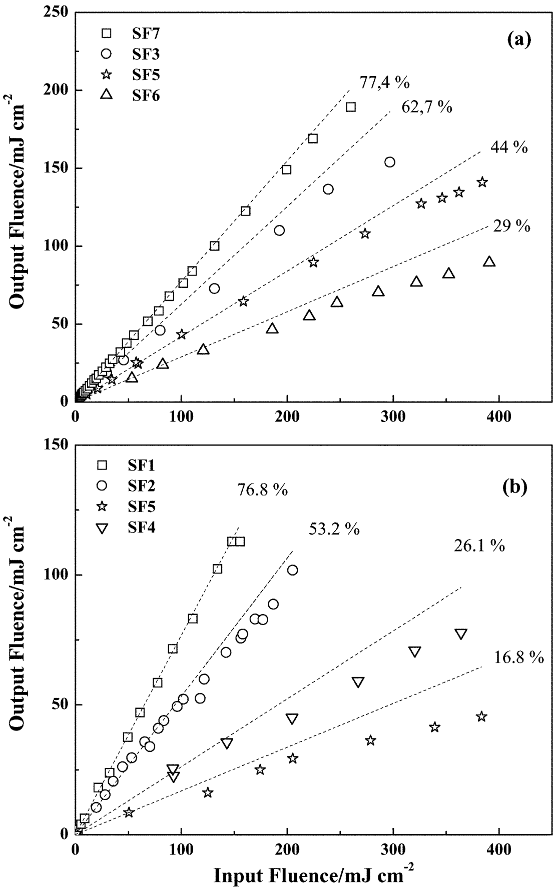

Fig. 2 Optical limiting response of various C_{60}–PS_x films for (a) 10 ns, 532 nm pulses and (b) 500 fs, 496 nm pulses.

Fig. 2(a) and 2(b) display the optical limiting response of various samples containing different C_{60} concentrations under 10 ns, 532 nm and 500 fs, 496 nm laser excitation respectively, where the dashed lines correspond to linear transmission. As can be seen, the threshold for optical limiting of the samples lies in a range 65–150 mJ cm^{-2}, comparable to that of C_{60} and C_{60}–polystyrene star polymer toluene solutions,[1,10,34] the limiting effect being more efficient for higher concentrations. During these measurements special care was taken to avoid any photophysical modification of the polystyrene matrix. A damage threshold for polystyrene was observed of about 300 mJ cm^{-2}, the value depending on the sample, which drastically limited the range of fluences used in our experiments. As a result, no limiting plateau could be observed in the optical limiting action of the films under study, a response similar to that observed in PMMA films containing methano-C_{60} derivatives.[28]

The observed low damage threshold for polystyrene films was assigned to degradation of the polystyrene chain, which easily undergoes photo-oxidation *via* a two-photon absorption of the 532 nm and 496 nm photons.[47] The photo-oxidation product has a red shifted absorption and an enhanced ground state cross section around 250 nm, compared to the non-oxidized PS chain.[47] This iterative absorption process results in the material having a sharp damage threshold, the accumulative photo-destruction appearing after a few laser pulses. Other explanations could arise from a thermal load to the matrix since recent studies have reported relaxation of the first excited singlet state (S_1) not only by intersystem crossing but also by the interaction of C_{60} molecules with the embedding matrix.[25] However, in the case of femtosecond excitation, where the damage threshold was roughly the same as in the nanosecond regime, two of the samples (SF4 and SF5), embedding quite high concentrations of C_{60} (37.9 mM and 6.56 mM respectively), were not destroyed by an input fluence as high as 800 mJ cm^{-2} (SF4) and 1 J cm^{-2} (SF5). Indeed, for all the samples, those containing less C_{60} (and so containing relatively more PS) were more fragile than the more concentrated ones. This fact seems to denote that the PS matrix is mainly responsible for the photo-degradation of the films. Nevertheless, all nonlinear optical measurements reported here were conducted below the damage threshold fluence, since one must avoid permanent changes in the linear optical properties of the samples during irradiation which could result in illusory symmetrical Z-scan transmission curves leading to higher values of nonlinear absorption parameter β.[48]

For a better understanding of the nonlinear optical response, we define the limiting efficiency as the relative change of the normalized transmission $\Delta T/T_0$. Fig. 3(a) displays the variation of limiting efficiency with reduced C_{60} concentration for all the films studied and for 1 mM toluene solutions of C_{60}–$(PS_{17800})_6$ and C_{60} for comparison under ns excitation at 220 mJ cm^{-2}. The figure reveals the following: (1) the limiting efficiency of C_{60} is higher than both C_{60}–PS_6 solutions and films (even the very high concentration films); (2) C_{60}–PS_6 in solution has a response similar to the films; (3) the dependence of the limiting efficiency of the films on the reduced concentration does not follow the same trend over the whole range of concentrations studied: thus for the high concentration ($[C_{60}] > 5$ mM) samples (SF5, SF9, SF6, SF4), although these present better limiting efficiency, its increase as a function of concentration is less effective than that for the low concentration ($[C_{60}] < 5$ mM) samples (SF7, SF1, SF2, SF3, SF10).

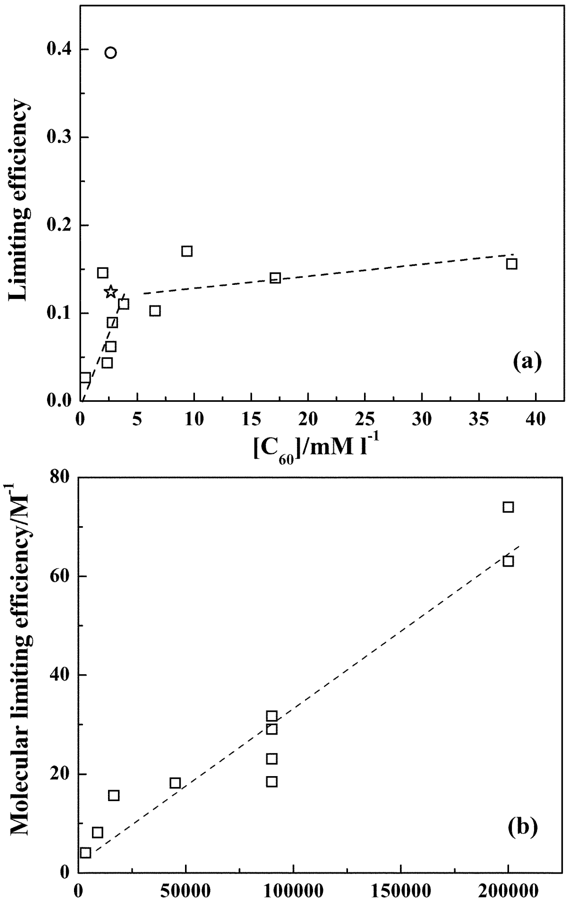

Fig. 3 (a) Limiting efficiency, defined as the relative change of the transmission $\Delta T/T_0$ as a function of the reduced C_{60} concentration and (b) molecular limiting efficiency defined as the ratio of the limiting efficiency over the reduced C_{60} concentration as a function of the MW of the arms for 10 ns, 532 nm laser excitation. Squares correspond to the films, the circle to the C_{60} solution and the star to the C_{60}–$(PS_x)_y$ solution. Dashed lines are given as guides to the eye.

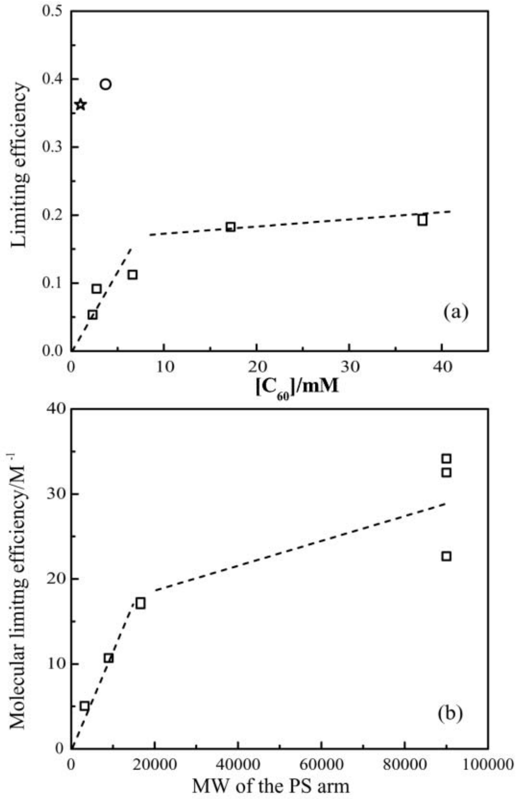

Fig. 4 (a) Limiting efficiency defined as the relative change of the transmission $\Delta T/T_0$ as a function of the reduced C_{60} concentration and (b) molecular limiting efficiency defined as the ratio of the limiting efficiency over the reduced C_{60} concentration as a function of the MW of the arms for 0.5 ps, 496 nm laser excitation. Squares correspond to the films, the circle to the C_{60} solution and the star to the C_{60}–$(PS_x)_y$ solution. Dashed lines are given as guides to the eye.

Fig. 3(b) presents the molecular limiting efficiency, defined as the ratio of the limiting efficiency to the reduced C_{60} concentration, as a function of the MW of the arm. As we can see, the molecular limiting efficiency increases with the length of the PS arms.

A similar response was found under sub-ps excitation. Fig. 4(a) and 4(b) present the dependence of the limiting efficiency on the reduced C_{60} concentration and the molecular limiting efficiency as a function of the MW of the arms respectively, recorded under 0.5 ps, 496 nm laser excitation. As can be seen, both C_{60} and C_{60}–$(PS_x)_y$ in solution exhibit higher limiting action than all films studied. In addition, the variation of the limiting efficiency on the reduced concentration does not follow the same dependence over the whole range of concentrations studied, a response similar to that observed under ns excitation. Finally, the molecular limiting efficiency increases with the MW of the arms.

In order to determine the nonlinear absorption parameter of the samples, several Z-scan experiments were performed for each sample at several intensities. Fig. 5 shows a typical open-aperture Z-scan transmission curve for the SF4 sample, obtained under 10 ns, 532 nm laser irradiation. The nonlinear absorption parameter β can be deduced by fitting the experimental results of Fig. 5 with the following formula:[40]

$$T_{\mathrm{Norm}}(z) = \frac{\ln\left[1 + \frac{\beta L_{\mathrm{eff}} I_{00}}{1+(z/z_0)^2}\right]}{\frac{\beta L_{\mathrm{eff}} I_{00}}{1+(z/z_0)^2}} \qquad (1)$$

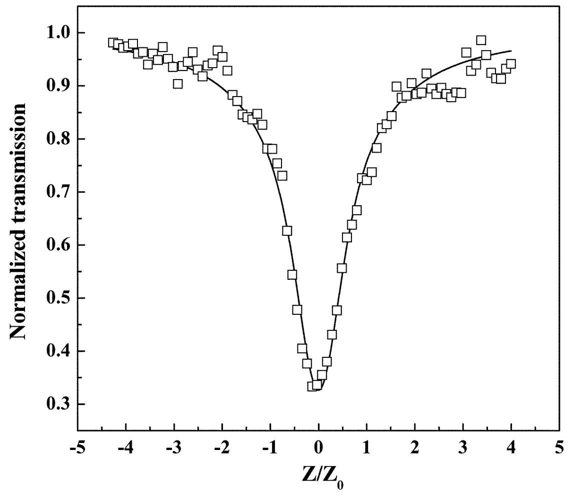

Fig. 5 Open aperture Z-scan for sample SF4, obtained under 10 ns, 532 nm laser irradiation.

where $L_{\text{eff}} = (1/\alpha_0)\{1 - \exp(-\alpha_0 L)\}$ is the effective absorption length, L being the thickness of the film and α_0 the linear absorption coefficient, z_0 is the Rayleigh length and I_{00} is the maximum incident intensity at $z = 0$. The estimated β values for all films studied are presented in Fig. 6(a) and 6(b) as a function of the reduced C_{60} concentration for 10 ns, 532 nm and 500 fs, 496 nm laser excitation respectively. As shown, the Z-scan experimental results exhibit similar trends to those found in the case of the optical limiting efficiency depicted in Fig. 3(a), 3(b), 4(a) and 4(b).

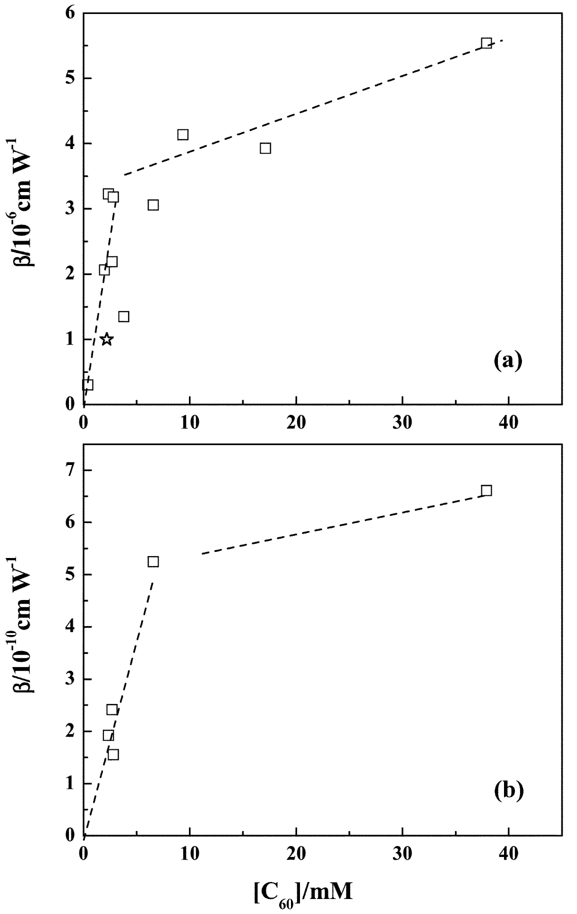

Fig. 6 Nonlinear absorption coefficient β as a function of the reduced C_{60} concentration of all the samples studied for (a) 10 ns, 532 nm pulses and (b) 500 fs, 496 nm pulses. Dashed lines are given as guides to the eye.

Discussion

As shown in Fig. 6(a) and 6(b), the β values obtained for the C_{60}–$(PS_x)_y$ films are of the same order of magnitude as those obtained for the C_{60} solutions, for both laser pulse durations used. In the nanosecond case, the limiting efficiency appears to be fluence dependent since triplet excited states are involved in the nonlinear absorption. Under sub-ps excitation, where both excited state involvement and resonant electronic polarizability are no doubt relevant, the required intensity to obtain the same limiting efficiency is three orders of magnitude larger than that of the ns case, although the fluence ranges are of the same order of magnitude. This result is similar to that observed for C_{60}–toluene solutions in previous studies where both laser pulse durations[42,49] have been used.

As mentioned previously, the relatively lower limiting efficiency of the star-polymer films under nanosecond excitation can be understood on the basis of the lower triplet state formation yield and its shorter lifetime in the case of the films. The shortening of the triplet state lifetime does not seriously affect the limiting action, in so far as it remains much longer than the excitation laser pulse used. In that respect, although the triplet state lifetimes in film and in solution differ by an order of magnitude, the relative responses of both solutions and films are quite similar. However, it is not yet clear what changes actually occur in going from the C_{60}–$(PS_x)_y$ molecular state to the C_{60}–$(PS_x)_y$ solid film state. It appears, from the observed multiple slopes of both Fig. 3(a) and 6(a), with respect to the concentration of C_{60}, that inter-C_{60} core and/or inter PS-arm interactions play noticeable roles. The rupture in the linear dependence of both limiting efficiency and β suggests that above a certain concentration threshold (*e.g.* ~5 mM), stronger intermolecular interactions might occur, which add further relaxation pathways resulting in the reduction of the triplet state relative population and correlatively the nonlinear absorption efficiency. In Fig. 3(b), since the limiting efficiency increases with the length of the graft, it is clear that in the set of samples that we have studied, the length of the arm is a factor that determines the closeness of approach between each C_{60}–$(PS_x)_y$ molecule, and in this way the intermolecular interactions. Moreover, this tendency seems to be valid regardless of the amount of added PS arms used to plasticize the film. However, even though we do not possess any direct experimental evidence, it seems that other deexcitation channels and photophysical mechanisms can probably occur when the absolute concentration of C_{60} increases considerably.

Concerning the femtosecond results, where both excited states and resonant electronic polarizability can be responsible for the nonlinear absorption effects, the decreased optical limiting efficiency and NLO absorption parameter with the concentration indicate that, as in the nanosecond case, intermolecular interaction could play a significant role. In this case, the proximity of the arms of a neighboring molecule or the C_{60} cage itself could induce a modification in the delocalization and polarizability of the π electron clouds responsible for the electronic nonlinear response, giving rise to a decrease in the nonlinear optical absorption of the films.

Conclusion

We have carried out measurements of the nonlinear optical absorption properties of C_{60}–$(PS_x)_y$ based solid films, the C_{60}–star polymers in the films having different molecular weights and various numbers of PS arms (x = 2, 4 and 6). We have confirmed that with these macromolecules, films can be formed containing a high concentration of C_{60} fullerene molecules (equivalent to a solution of up to 37 mM in our case) and so enhancing the third order nonlinear optical properties. We have, however, found a concentration threshold of about 5 mM beyond which improvement in nonlinear optical properties diminishes due to intermolecular interactions. This behavior is correlated, for the set of samples used here, with the length of PS graft, which prevents intermolecular interactions between the C_{60} moieties. We have also shown that the two-arm C_{60}–PS_2 entity, which possesses recognizable residual bands of the C_{60} absorption spectrum, behaves better than those having 4 or 6 PS arms, for which the C_{60} spectral features are absent. Moreover, polystyrene was shown not to be the best matrix as the damage threshold is rapidly reached. Studies on other matrices and further photophysical properties have to be carried out to improve the nonlinear optical properties of such promising macromolecules up to the optical level of quality required for practical nonlinear optical device applications.

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