Optical Limiting Property of Polystyrene-Bound C_{60}

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Optical limiters exhibit a fixed intensity of transmitted light at high incident light levels. The limiter can serve as protecting sensor and eye. The C_{60} solution shows the excellent optical-limiting property compared with many other optical-limiting materials.[1] For optical-limiting application, a solid-state optical limiter is desirable, but the performance of C_{60} in poly(methyl methacrylate) as a solid polymer was low compared with that of the C_{60} solution.[2] Here we described the optical-limiting study of a solid-state polystyrene-bound C_{60} and demonstrated that this polymer improved the optical-limiting performance of the C_{60} solution. The polymer was created by a high-pressure polymerization of styrene in the presence of C_{60}. The optical-limiting tests were performed with a pulse laser beam at 532 nm, and the limiting was about 5 times greater than that of a C_{60} solution.

Buckminsterfullerene (C_{60}) is a soluble new form of carbon[3] and can be obtained by evaporating graphite electrodes in an atmosphere of ~100 Torr of helium.[4] The combination of this molecule with polymer is challenging. The polymeric fullerene derivatives were prepared in the previous papers.[5–7] We expected that the optical clear polymer-bound C_{60} would be a very useful support for optical-limiting applications. Polystyrene is known to be an amorphous transparent polymer. Polymeric fullerene based on polystyrene was reported in 1992.[5] The polymeric fullerene was synthesized by addition of polystyrene carbanion solution into the C_{60} solution. Unsaturated compounds such as acetylene and diphenyldiacetylene were polymerized by the reaction-induced high pressure.[8,9] As C_{60} and styrene are both unsaturated compounds, pressure transforms a styrene solution of C_{60} into the polystyrene-bound C_{60}, as shown below.

C_{60} (C_{60}: 99.9%) from MER Corp. was used without further purification and was easily soluble in styrene. Reaction of the styrene solution of C_{60} under high pressure was carried out using a high hydrostatic pressure reactor shown in the previous paper.[9] The solution of 0.1 wt % C_{60} in styrene was packed into a poly(tetrafluoroethylene) cell and introduced into the high-pressure vessel. The specimen was compressed at various pressures in the range of 0.1–0.4 GPa by a hand oil pump with a pressure-transmitting medium (silicone oil) and substantially reacted at room temperature (22–25 °C) for 20 and 180 h. After reaction under high pressure, the liquid product was obtained. The visible absorption spectrum for the liquid product reacted under 0.4 GPa for 20 h is shown in Figure 1. For comparison purposes, the spectrum of the styrene solution of C_{60} is included in the figure. The styrene monomer was a colorless, transparent liquid and had no absorption in the visible region. The absorption maximums are found to be 407, 540, and 598 nm for the styrene solution of C_{60}. There is a continuous absorption for the specimen reacted under 0.4 GPa for 20 h in the visible region from 400 to 800 nm, as shown in Figure 1. The absorbance was weaker at longer wavelengths. This suggests that the specimen has a number of chromophores which have different absorption maximums according to the length of the conjugated system due to the reaction of C_{60} with styrene monomer. The absorbance of the liquid product in the visible region increased with pressure and time, [pressure, 0.1–0.4 GPa; absorbance at 450 nm, 0.1–0.366 (time, 20 h)] and [time, 20, 180 h; absorbance at 450 nm, 0.1, 0.5 (pressure, 0.1 GPa)], where the absorbance of the styrene solution at 450 nm was 0.060.

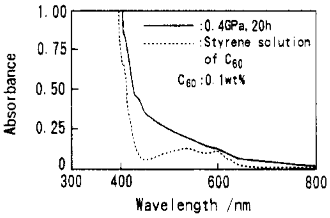

Figure 1. Visible absorption spectra of the liquid product reacted under 0.4 GPa at room temperature for 20 h and the styrene solution of C_{60} (specimen path length: 1 mm).

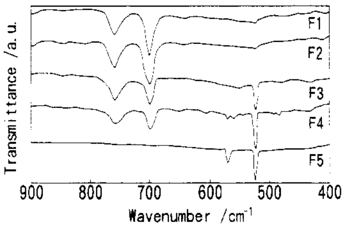

Figure 2. IR spectra of products reacted under 0.1 GPa at room temperature for 180 h (components: F1–F5).

After evaporation of unreacted styrene monomer from the liquid product reacted under 0.1 GPa for 180 h, the solid product (0.3 wt %) was obtained. Gel permeation chromatography of the product gave four peaks at the elution times of 31, 59, 63, and 81 min. The characterization of the solid product was carried out by separation of five components by gel permeation chromatography (elution time of F1, 28–33 min; elution time of F2, 33–44 min; elution time of F3, 44–61 min; elution time of F4, 61–72 min; elution time of F5, 72–92 min). GPC chromatograms of the styrene and C_{60} indicated the peaks at the elution times of 62 and 81 min, respectively. It is suggested that the product does not have styrene monomer but C_{60}. Figure 2 shows the infrared spectra of the components. The spectrum of component F5 corresponded to that of C_{60}. The absorption intensity at 528 cm^{-1} increases with an increase of elution time (decrease of molecular weight). As substituted C_{60} has a strong absorption band in the 520–530 cm^{-1} region,[10] the IR band at 528 cm^{-1} of components F1–F4 whose molecular weights are larger than that of C_{60} is due to the polystyrene-bound C_{60}. The bands at 755 and 698 cm^{-1} indicate a monosubstituted benzene structure of styrene polymer and polystyrene-bound C_{60}. We find that C_{60} was reacted with styrene polymer under high pressure.

The solid-state product was only obtained by reacting C_{60}/styrene solution (C_{60} content: 0.2 wt %) under a high pressure of 0.1 GPa at 200°C for 5 h. Figure 3 shows the three-dimensional GPC chromatogram of the product as a function of wavelength and elution time. The chromatogram between 22 and 25.3 min shows the UV and visible absorption from 250 to above 400 nm. The chromatogram of C_{60} is obtained at 36.5 min of the

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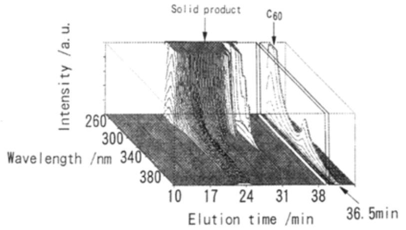

Figure 3. Three-dimensional GPC chromatograms of product reacted under 0.1 GPa at 200 °C for 5 h and C_{60} (mobile phase: chloroform).

elution time and exhibits the UV and visible absorption from 250 to above 400 nm (Figure 3). Unreacted C_{60} is not observed from the product in the chromatogram. The styrene polymer absorbed UV below 320 nm, and the elution time was shorter than that of the monomer (34.6 min). Thus, for the product, the chromatogram at the lower elution time (22−25.3 min) indicates the presence of polystyrene-bound C_{60}. Based on the polystyrene calibration, the molecular weight of the polystyrene-bound C_{60} was 22 000−300 000. The chromatogram observed with the UV detector at the elution time (25.3−32.9 min) is attributed to the styrene polymer (molecular weight: 170−22 000). The solid-state product was characterized using a ^{13}C NMR spectrum in $CDCl_3$. Pure C_{60} exhibited a resonance at 143.3 ppm. The product exhibited resonances between 30 and 50 ppm (37.2, 40.4, 43.9 ppm) due to the sp^3-carbon. The aromatic region of the product (sp^2-carbon) shows resonances in the range 120−150 ppm (125.6, 127.9, 140.9, 142.3, 145.2 ppm). Polystyrene exhibited resonances at 40.4, 43.8, 125.6, 128.0, and 145.3 ppm. The resonances at 37.2, 140.9, and 142.3 ppm are attributed to the covalent bonding between the styrene unit and C_{60}. Thus the product was a mixture of polystyrene and polystyrene-bound C_{60}.

A circular disk of the product with the polystyrene-bound C_{60} (mixture of polystyrene and polystyrene-bound C_{60}) was cut from the solid specimen. The disk was 1 mm in thickness and 8 mm in diameter. The solid specimen was orange and was different from C_{60} in magenta liquid solution. The optical-limiting tests were performed with a frequency-doubled Nd:YAG laser that produces an 8 ns pulse width. The laser was operated at 10 Hz. The circular disk was irradiated with pulses of 1 mm in diameter using an aperture. The input energy was increased with a decrease in delay time of the Q-switch. The pulse width was approximately independent of the delay time. The beam was relatively collimated as it passed through the sample, and the intensity was approximately spatially constant. Input and output energies per pulse were measured with a power meter. The transmittance at 532 nm using a spectrophotometer decreased from 55 to 20% upon reaction of the styrene solution of C_{60} under high pressure. This change in transmittance was due to a change in the absorption spectrum. Figure 4 shows the input−output response of the solid specimen at a concentration of 0.2 wt %. At low input fluence (0.1 J/cm^2), the transmittance is low (10%) compared with that obtained by the spectrophotometer (20%). The transmittance decreases with input fluence, and we observe an optical-limiting property with saturated output fluence of 0.026 J/cm^2. The damage input fluence of the solid was 0.6 J/cm^2. For comparison purposes, Figure 4 also shows the input−output response of the styrene solution of C_{60} (C_{60}: 0.2 wt %). The C_{60} dispersed in toluene also showed the an input−output response similar to that of the styrene solution. The styrene solution of C_{60} and the solid product have the same concentration of C_{60} and specimen path length, but the optical-limiting property of the solid specimen was about 5 times greater than that of the styrene solution. The solid specimen of polystyrene-bound C_{60} had a high optical-limiting property compared with C_{60}. The reverse saturable absorption mechanism (excited state absorption mechanism) yielded a reasonable explanation for the optical limiting of C_{60}.[11] C_{60} exhibits absorption from excited electronic states to higher electronic states subsequent to excitation. This excited state absorption involves a singlet−singlet or triplet−triplet transition. To obtain the optical-limiting property, the upper singlet and lower triplet must have larger absorption cross sections than the ground state. Those absorption cross sections of C_{60} seem to be increased by binding C_{60} with polystyrene. The ground state absorption changes from a 55% transmitting solution to a 20% solid product at 532 nm. This is an absorbance change of 0.26−0.7. This is almost a factor of 3 change in the ground absorption and is semiequivalent to adding a filter to the input intensity before adding nonlinear effects. This could account for a large portion of the 5-fold increase. Another possibility is that the excited state absorption increase at 532 nm may be due to a different shift of the excited state absorption peak relative to the shift observed for the ground state peak and no actual increase in the maximum excited absorption has actually occurred.

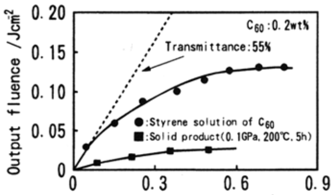

Figure 4. Relationship between output fluence and input fluence of the solid product with polystyrene-bound C_{60} together with the solution of C_{60} in styrene (path length for the solution: 1 mm).

In conclusion, the optical-limiting property of the solid product with polystyrene-bound C_{60} was about 5 times greater than that of a C_{60} solution.

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