Synthesis and Optical Properties of Fullerene-Functionalized Polycarbonates

Ben Zhong Tang,* Han Peng, Shuk Mei Leung, Cheuk Fai Au, Wan Hong Poon, Huilin Chen, Xuanzheng Wu, Man Wah Fok, Nai-Teng Yu, and Hiroyuki Hiraoka

Department of Chemistry, Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong

Chunying Song, Jishi Fu, Weikun Ge, and George K. L. Wong

Department of Physics, HKUST, Clear Water Bay, Kowloon, Hong Kong

Takashi Monde and Fujito Nemoto

Central Research Laboratory, Neos Company, Ltd., Kosei-Cho, Koga-Gun, Shiga 520-32, Japan

Kai C. Su

Technology Resource International Corporation, 5000 McGinnis Ferry Road,
Alpharetta, Georgia 30202

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ABSTRACT: Fullerenation of polycarbonate (PC) is achieved by direct reaction of C_{60} with PC using $AlCl_3$ as catalyst. Stirring a 1,1,2,2-tetrachloroethane solution of C_{60} and PC in the presence of $AlCl_3$ under nitrogen at 140 °C for 24 h attached C_{60} to the PC chains, yielding fullerenated PCs (C_{60}−PCs) with a C_{60} content up to 2.16 wt %. The C_{60}−PCs are soluble in tetrahydrofuran (THF) and chloroform, and IR, UV, and NMR analyses suggest that they possess the molecular structure $H_xC_{60}(PC)_x$ with $x < 1$ on the average. The C_{60}−PCs limit strong 532-nm optical pulses more effectively than the parent C_{60}. Light transmission spectra of the C_{60}−PC solutions red-shift with increasing concentration, with their cutoff wavelengths predictably tunable by simply changing their concentrations.

Introduction

Since diamond and graphite have long been the only known forms of carbon, the discovery of fullerene, a new carbon allotrope, has fascinated the scientific community, and the properties of fullerenes have understandably been a focus of intensive research.[1] Novel properties of fullerenes include superconductivity, ferromagnetism, and optical nonlinearity.[2] The poor tractability of the fullerenes, however, has been an obstacle for converting fullerenes from laboratory curiosities to practically useful materials.

Synthesis of fullerene polymers is of interest from the viewpoints of both basic research and practical applications: It will not only widen our understanding on the basic chemistry of the fullerene molecules but also contribute to the development of processable fullerene-based specialty materials.[3] Synthetic strategies for preparing soluble C_{60}-containing polymers include (i) copolymerizations with reactive monomers (M)

$$C_{60} + n\mathrm{M} \rightarrow C_{60}(\mathrm{M})_n \quad (1)$$

and (ii) polymer reactions with soluble preformed polymers (P)

$$C_{60}\mathrm{X} + \mathrm{PY} \rightarrow C_{60}\mathrm{XYP} \quad (2)$$

$$C_{60} + \mathrm{P} \rightarrow C_{60}\mathrm{P} \quad (3)$$

where X and Y denote the mutually reactive functional groups attached to C_{60} and polymer. Because of C_{60}'s strong inhibiting power,[4] the number of monomers (M in eq 1) that can directly copolymerize with C_{60} is limited. The polymer reaction in eq 2 is an *indirect* reaction because the fullerenation is realized through the reaction of prefunctionalized C_{60} (C_{60}X) and polymer (PY). The preparation of C_{60}X and/or PY sometimes requires painstaking synthetic efforts, which in turn limits the scope of applicability of the indirect fullerenation methodology. Fullerenation by *direct* reaction between C_{60} and polymer themselves (eq 3) is probably the most "economic" way for incorporating C_{60} cages into polymer chains. Not much work, however, has been devoted to the development of direct fullerenation reactions. Olah et al. have made a pioneering contribution to the area, in which they employed an elegant $AlCl_3$-catalyzed fullerenation reaction to attach C_{60} cages to the aromatic rings of polystyrene, although the fullerenation products are highly cross-linked.[5] Sun and co-workers were able to prepare soluble C_{60}-containing polystyrene using the $AlCl_3$ catalyst, but once the products were dried, they could not be dissolved.[6] Almost all fullerenated polymers prepared so far by different reactions are chain-growth polymers,[3] fullerenation of step-growth polymers remains a virtually unexplored research area.

Step-growth polymers have enjoyed a broad spectrum of applications in high-technology industries as, e.g., thermotropic and lyotropic liquid crystals (LC), orientation layers in LC display systems, and high-temperature nonlinear optical materials.[7] Fullerenation of step-growth polymers is thus of technological interest. In this study, we chose polycarbonate (PC), a typical step-growth polymer and also an excellent optical plastic, as a model polymer for studying the $AlCl_3$-catalyzed fullerenation of step-growth polymers. The fullerenation of

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Table 1. $AlCl_3$-Catalyzed Fullerenation of PC[a]

						fullerenated PC				
									C_{60} content	
no.	C_{60}/PC feed ratio (wt %)	$AlCl_3$ (g/mL)	solvent	temp (°C)	time (h)	yield (%)	M_w[b]	PDI[b]	(wt %)[c]	(no./chain)[d]
1	0.54	0.010	THF	rt[i]	72	ni[e]				
2	1.26	0.006	$CHCl_3$	rt[i]	24	ni[e]				
3	2.01	0.11[f]	(solid)	260	0.1	16.5[g]	7000[g]	1.1	nd[h]	
4	0.98	0.013	$(CHCl_2)_2$	140	24	97.2	13600	2.6	1.23	0.09
5	2.82	0.021	$(CHCl_2)_2$	140	24	78.7	24600	2.7	1.46	0.18
6	5.44	0.014	$(CHCl_2)_2$	140	24	100	29900	1.4	2.16	0.64

[a] Stirred under nitrogen in the presence of $AlCl_3$. [b] Determined by GPC (RI detector) on the basis of a polystyrene calibration. PDI: polydispersity index (M_w/M_n). For the starting PC, $M_{w,o} = 33\,400$, $PDI_o = 2.4$. [c] Estimated by UV analysis at 350 nm. [d] Estimated from the M_n data. [e] Not isolated. [f] In the unit of gram. [g] For the THF-soluble fraction. [h] Not determined. [i] room temperature.

PC might be difficult because the electronic effect of the functional carbonate group may slow down or even inhibit the fullerenation of the polymer. Indeed, aromatic compounds with polar substituents such as anisole and *N*,*N*-dimethylaniline do not react with C_{60} in the presence of $AlCl_3$.[5a] However, if we can overcome the difficulties involved, this will open up a new avenue for directly fullerenating a wide range of technologically important high-performance polymers because aromatic rings with polar functional groups are important building blocks in the molecular architecture of step-growth polymers. Furthermore, because the C_{60} cages are attached to an aromatic polymer chain, the C_{60}−PCs may possess novel optical properties due to the $\pi-\pi$ electronic interaction between the conjugated ring systems.

We report here our results on fullerenating PC using $AlCl_3$ as a catalyst. As anticipated, the fullerenation was not easy, but we succeeded in defining reaction conditions to have the fullerenation proceed in a controlled manner. The fullerenated PCs are soluble in common organic solvents, possess enhanced optical limiting power, and exhibit novel bathochromic light transmission characteristics.[8]

Experimental Section

General Details. High-purity (99.95%) C_{60} was purchased from MER and kept in a dark place before use. PC was purchased from Aldrich and was further purified by repeated precipitation. Anhydrous $AlCl_3$ (99%) was from Acros. The solvents (Aldrich) were mostly purified by distillation prior to use. All reactions were carried out under nitrogen. The ^{1}H and ^{13}C NMR spectra were recorded on a Brucker ARX300 spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in parts per million (ppm) on the δ scale referenced to $SiMe_4$ (TMS), and coupling constants (J) are expressed in hertz. The FT-IR spectra were measured on a Perkin-Elmer 16PC spectrophotometer (KBr). The UV−vis absorption and transmission spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer using a 10-cm square quartz cell. The molecular weights (MWs) of the polymers were estimated by a Waters gel permeation chromatograph (GPC) system. Degassed tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min. The working wavelength of the UV detector in the GPC system was set at 340 nm. A set of 12 Waters monodisperse polystyrene standards were used for calibration purpose. Under nitrogen, the thermal stability of the C_{60}−PCs was evaluated on a Perkin-Elmer TGA 7 thermogravimetric analyzer at a heating rate of 10 °C/min, and the transition thermograms were recorded on a Setaram DSC 92 differential scanning calorimeter at a heating rate of 20 °C/min.

Reaction Procedures. In a typical run, a baked 50-mL flask was charged with 508.2 mg of PC, 5.0 mg of C_{60}, and 10 mL of 1,1,2,2-tetrachloroethane. The resulting homogeneous solution was transferred by a syringe to another baked 100-mL flask containing 134.0 mg of $AlCl_3$ under nitrogen at room temperature with stirring. The content was then heated to 140 °C, and the initial purple color of the mixture gradually changed to dark brown in ca. 30 min. After stirring at 140 °C for 24 h, the mixture was cooled to room temperature and a small aliquot was taken out and precipitated into 5 mL of hexane, a solvent for C_{60}.[9] UV analysis of the hexane supernatant showed no absorption peaks from unreacted C_{60}. After the confirmation of the complete consumption of C_{60}, the reaction mixture was quenched by the addition of a few drops of a water/THF mixture. The quenched reaction mixture diluted with CH_2Cl_2 was transferred to a separation funnel and washed with water (3×). The organic layer was collected and dried over anhydrous Na_2SO_4 overnight with stirring. After filtration, the solvent was evaporated, leaving a brown film on the wall of the evaporation flask. The film was redissolved in ca. 20 mL of THF, and the polymer was reprecipitated into 1 L of hexane. The product was filtered off and dried at room temperature in vacuo to a constant weight. A brown powder was obtained in 97.2% yield, whose C_{60} content was estimated to be 1.23 wt % using a UV calibration curve.[10] $M_w = 13\,600$, $M_w/M_n = 2.6$ (GPC). IR (KBr, ν): 3429 (br), 3040 (w), 2968 (s), 1778 (vs), 1602 (m), 1506 (s), 1410 (m), 1386 (w), 1364 (m), 1228 (vs), 1194 (s), 1162 (s), 1080 (s), 1016 (s), 888 (m), 830 (s), 768 (m), 556 (s), 528 (vw) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS, ppm): δ 7.25 (J = 8.76), 7.16 (J = 8.67), 3.95, 3.87, 1.68. ^{13}C NMR (75 MHz, $CDCl_3$, TMS, ppm): δ 152.10, 148.93, 148.23, 127.88, 126.38, 120.29, 42.52, 30.88. UV (THF, λ_{max}): 237.5, 258.1 (sh), 263.7, 286.5 (sh), 328.7 (sh) nm.

Optical Limiting Measurements. The limiting experiments were performed at 532 nm with 8-ns pulses from a frequency-doubled Q-switched Nd:YAG laser (Quanta Ray GCR-3) operating in a near-Gaussian transverse mode with a repetition rate of 10 Hz. The pulsed laser beam was focused into a 1-cm square quartz cell filled with a THF solution of C_{60}−PC (or a toluene solution of C_{60} in the control experiment). The incident and transmitted energies were measured by an OPHIR detector (30-A-P-Diff-SH), and every point of the optical limiting data was the average of at least 15 laser shots. The detector was connected to a computer both before and after the optical limiting measurements were run, and the output stability of the laser equipment was double checked by taking a series of output data by the energy meter every 10 s for an extended period of time.

Results and Discussion

Fullerenation Reaction. Olah et al.[5] and Sun's group[6] fullerenated polystyrene using $AlCl_3$ as catalyst at room temperature in CS_2. Because PC is not soluble in CS_2, we attempted to fullerenate PC in THF. Stirring a mixture of PC/C_{60}/$AlCl_3$ in THF at room temperature for several days, however, showed no sign of reaction (Table 1, no. 1). No reaction took place in $CHCl_3$. To check whether the fullerenation of PC is completely inhibited, we heated a mixture of PC, C_{60}, and $AlCl_3$ at 260 °C under nitrogen. The color of the mixture quickly

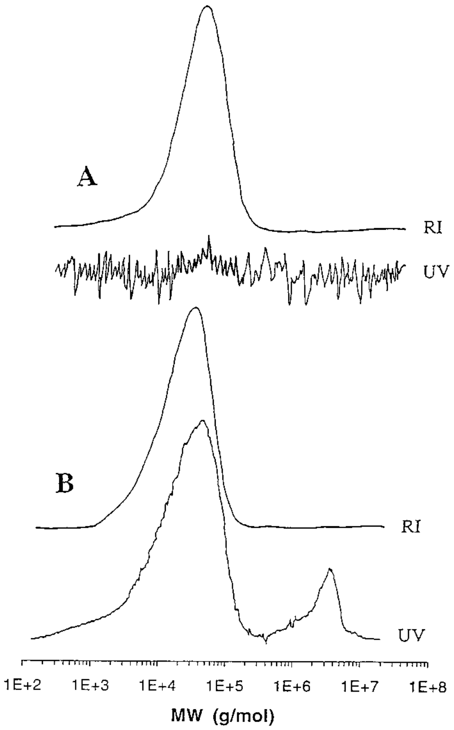

Figure 1. GPC traces of THF solutions of (A) PC and (B) C_{60}–PC (sample from Table 1, no. 4). Working wavelength of the UV detector in the GPC system: 340 nm.

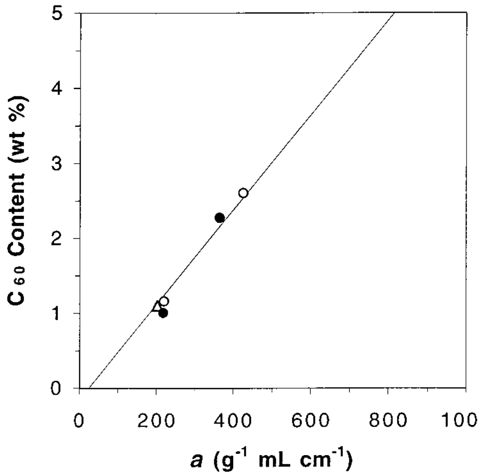

Figure 2. Plot of C_{60} content against absorptivity (*a*) at 350 nm, of THF solutions of C_{60}–PCs (filled circles; samples from Table 1, nos. 4 and 6). Data for the C_{60}–PCs prepared by the UV-induced (open circles) and AIBN-initiated (open triangle) fullerenation reactions are shown for comparison.[10]

changed to black, but most of the products were insoluble (Table 1, no. 3). Although the result of the high-temperature solid-state reaction is not satisfactory, it proves that PC can be fullerenated in the presence of $AlCl_3$.

We thus tried to optimize the reaction conditions in order to prepare soluble C_{60}–PCs in a controlled manner. As the preliminary experiments suggest, a relatively high temperature is needed to effect the $AlCl_3$-catalyzed fullerenation of PC. Because 1,1,2,2-tetrachloroethane is a good solvent of PC, C_{60}, and $AlCl_3$ with a relatively high boiling point (147 °C), we carried out a reaction in this solvent at 140 °C. The color of the reaction mixture quickly changed from purple to dark brown. The distinct color change was a sign of the expected reaction because Olah[5] and Sun[6] reported that the color of their $AlCl_3$-catalyzed fullerenation mixtures was dark (reddish-) brown. After 24-h reaction, the mixture was quenched and then precipitated into hexane. The hexane supernatant was colorless, confirming the complete consumption of the C_{60} reactant. While the starting PC is white, the purified reaction product was brown in color, suggesting the incorporation of the C_{60} cages into the PC chains. The UV detector (340 nm) in the GPC system hardly detected any peaks from the starting PC, whereas the reaction product gave two UV peaks, a strong peak in the "normal" MW region and a weak peak in the very high MW region (Figure 1). The fact that the product is soluble in THF reduces the likelihood of physical trapping of C_{60} inside the PC chains because THF is not a solvent of C_{60},[9] and the GPC data further confirm the covalent bonding between the C_{60} cages and the PC chains. The small UV peak in the very-high-MW region might correspond to the multiple addition product of PC to C_{60}. The $AlCl_3$-catalyzed fullerenation of aromatics is normally a fast reaction, yielding multiple addition products of general structure $H_xC_{60}Ar_x$ ($x = 12$ for major products in most cases) at room temperature in a short reaction time (2 h).[5] The fullerenation of PC was more difficult, and the amount of the very-high-MW multiple-addition product was also quite small because its existence could not even be detected by the RI detector. The MW of the product calculated from the RI peak ($M_w = 13\,600$; Table 1, no. 4) was lower than that of the starting PC ($M_{w,o} = 33\,400$) with almost no change in PDI, indicating that no heavy cross-linking but some chain cleavage was involved in the fullerenation reaction.

Since all of the C_{60} molecules had been consumed in the fullerenation reaction, we were able to calculate the C_{60} content of the reaction product on the mass basis. The UV data of the product fitted relatively well the calibration curve we previously established in our UV-induced and AIBN-initiated PC fullerenation systems (Figure 2).[10] We thus used the calibration curve to estimate the C_{60} content of the product, which was found to be 1.23 wt % (Table 1, no. 4). The average number of the C_{60} cages attached to a PC chain was quite small: 0.09; that is, only 9 fullerenes were attached to 100 PC chains on the average.

We tried to change the reaction conditions in order to incorporate more C_{60} cages into the PC chains. Increasing the C_{60}/PC feed ratio from 0.98 to 2.82 wt % increased the C_{60} content of the C_{60}–PC (Table 1, no. 5), but the increase was less than that of the feed ratio because not all of the C_{60} molecules were consumed after the 24-h reaction. A further increase in the feed ratio further increased the C_{60} content of the product to 0.64; i.e., about 6 out of 10 PC chains were fullerenated. We recovered the unreacted C_{60} and determined the C_{60} content of the C_{60}–PC on the mass basis. Its UV absorptivity data gave a good fit to the calibration curve in Figure 2, supporting the validity of using the calibration curve to estimate the C_{60} content of the C_{60}–PCs.

Structural Characterization. The products were characterized spectroscopically. C_{60} shows an IR absorption band at ca. 527 cm^{-1},[11] which often survives in the functionalization of the fullerene. As shown in Figure 3, the IR spectrum of the fullerenation product was essentially identical to that of the starting PC except for a new weak band at 528 cm^{-1}, suggesting that the C_{60} cages are covalently attached to the PC chains.

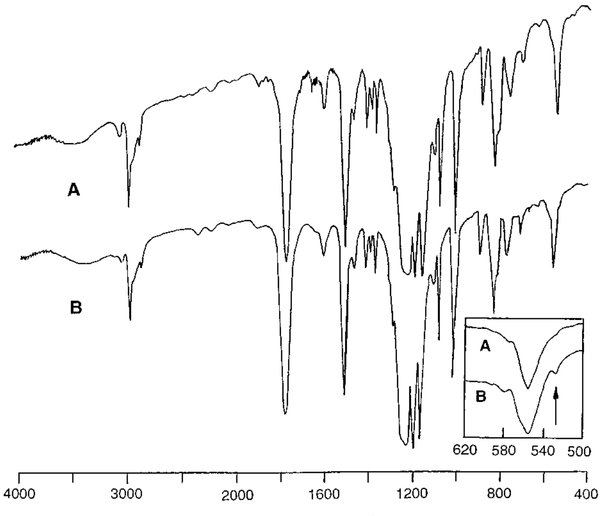

Figure 3. IR spectra of (A) PC and (B) C_{60}−PC (sample from Table 1, no. 6).

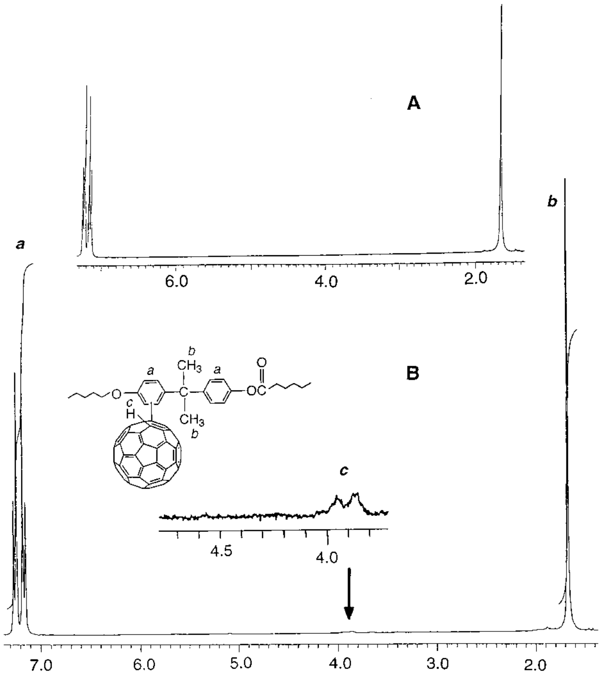

Figure 4. ^{1}H NMR spectra of $CDCl_3$ solutions of (A) PC and (B) C_{60}−PC (sample from Table 1, no. 6).

The solubility of the C_{60}−PCs in common organic solvents enabled the characterization of their molecular structures by solution spectroscopic methods. The ^{1}H NMR spectrum of the C_{60}−PC was similar to that of the starting PC (Figure 4). Two small new peaks appeared at ca. δ 3.9. Olah et al. assigned a broad peak in δ 3.4−5.4 to the allylic proton absorption of their polyarenefullerenes $H_xC_{60}(Ar)_x$.[5] West et al. observed that the fullerene skeletal protons in $H_{12}C_{60}[(SiMe_2)_3SiMe_2H]_{12}$ absorbed at ca. δ 3.5 and that those in $H_xC_{60}(SiMeO)_x[SiMe(n\text{-octyl})O]_{3x}$ absorbed at ca. δ 4.0 (two peaks).[12] It thus seems reasonable to assign the two peaks at δ 3.95 and 3.87 in Figure 4B to the absorption by the fulleryl protons in C_{60}−PC.

C_{60} absorbs at 257.9 nm, and PC absorbs at 262.8 nm. C_{60}−PC exhibited two peaks at 258.1 (sh) and 263.7 nm (Figure 5); i.e., it possesses the electronic transition characteristics of the two constituent parts: the C_{60} cages and the PC chains. Functionalization of fullerene often weakens or even completely eliminates the absorption peak of (pure) C_{60} at 328.4 nm, depending on the extent of reaction to the buckyball.[10] C_{60}−PC exhibited a weak but distinguishable peak at 328.7 nm. The UV data thus suggest that the extent of reaction to C_{60} is not high, in agreement with the low C_{60} content of the fullerenated PC (cf. Table 1).

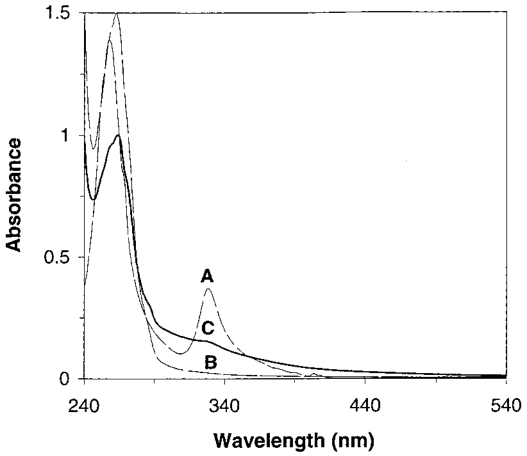

Figure 5. UV spectra of (A) C_{60}, (B) PC, and (C) C_{60}−PC (sample from Table 1, no. 6). Concentration (mg/mL)/solvent: (A) 0.011/hexane, (B) 0.475/THF, (C) 0.25/THF.

The C_{60}−PCs were thermally stable, losing no weight below 300 °C under nitrogen. The glass transition temperatures (T_gs) of the C_{60}−PCs measured by DSC were 126.3−127.5 °C, about 20 °C lower than that of the starting PC (146.0 °C). The low T_gs might be due to the chain cleavage involved in the fullerenation reaction. The plasticizing effect of the fullerenes may have also contributed to the decrease in the T_gs: When the extent of fullerenation to the PC chains and/or the degree of multiple addition of the PC chains to the C_{60} cages is low, the giant three-dimensional fullerenes may create large interchain free volumes, thus allowing segmental movements of the polymer chains to start at relatively low temperatures.[10]

Optical Properties. Control of light intensity in a predictable manner is one of the most important manipulations in optics engineering. An optical limiter is an intensity-sensitive nonlinear optical material that efficiently transmits weak light but strongly attenuates intense light. Development of optical limiters is a topic of great current interest because of the rapid advancement in the development of ultrafast high-power lasers and the growth in Space exploration.[13] C_{60} limits strong optical pulses based on a reverse saturable absorption mechanism because its excited-state absorption cross-section is larger than its ground-state absorption cross-section.[2a] However, the low absorption efficiency of C_{60} in the long-wavelength region due to its low solubility in common solvents has been an obstacle in finding practical applications for C_{60} as an optical limiter.[9,14] The C_{60}−PCs have better solubility than the parent C_{60}, which enables the preparation of high-concentration solutions. As shown in Figure 6, even at the same concentrations, the absorptivity of the C_{60}−PC solutions at 532.14 nm was higher than that of the C_{60}/toluene solutions. The concentrated solutions with high absorptivity would have well-populated excited states, and thus the C_{60}−PCs may exhibit superior optical limiting properties.

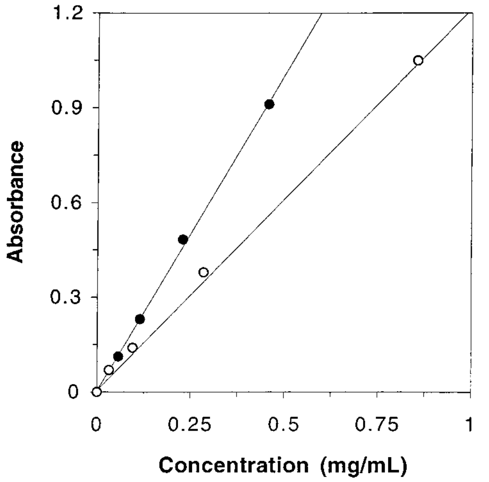

Figure 6. Comparison of absorptivity between THF solutions of C_{60}—PC (filled circles; sample from Table 1, no. 6) and toluene solutions of C_{60} (open circles) at 532.14 nm.

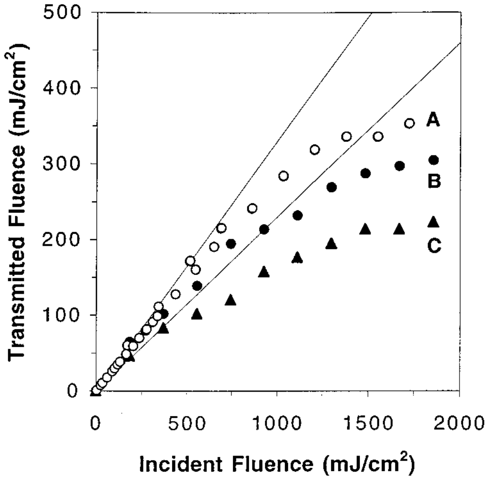

Figure 7. Optical limiting responses to 8-ns, 10-Hz pulses of 532-nm laser light, of THF solutions of C_{60}—PC (sample from Table 1, no. 6). Concentration (*c*, mg/mL): (B) 5.9, (C) 13.4. Linear transmittance (*T*, %): (B) 33, (C) 23. Data for a toluene solution of C_{60} (A) are shown for comparison: *c* (mg/mL), 0.11; *T* (%), 33.

Figure 7 shows optical limiting responses of THF solutions of a C_{60}—PC to 532-nm laser pulses. When a 5.9 mg/mL solution was exposed to optical pulses, the fluence transmitted from the C_{60}—PC solution increased linearly with the incident fluence in the low-fluence region (Figure 7B). The transmitted fluence started to deviate from linearity at an incident fluence of ca. 350 mJ/cm^2. The transmitted fluence leveled off at ca. 300 mJ/cm^2 (saturation fluence) when the incident fluence became very high. The transmittance from the C_{60}/toluene solution with the same initial optical density ($T = 33\%$) became nonlinear at an incident fluence of ca. 700 mJ/cm^2 and its saturation fluence was ca. 350 mJ/cm^2, both higher than those of the C_{60}—PC solution. Thus, C_{60}—PC is a better optical limiter than the parent C_{60}. The superior solubility of the C_{60}—PC allowed us to manipulate its optical limiting performance by simply changing its concentration. Thus, increasing the concentration of the C_{60}—PC solution lowered its saturation fluence to ca. 200 mJ/cm^2. Similarly, the THF solutions of the C_{60}—PCs with other C_{60} contents all performed better than the C_{60}/toluene solution in limiting the strong optical pulses.

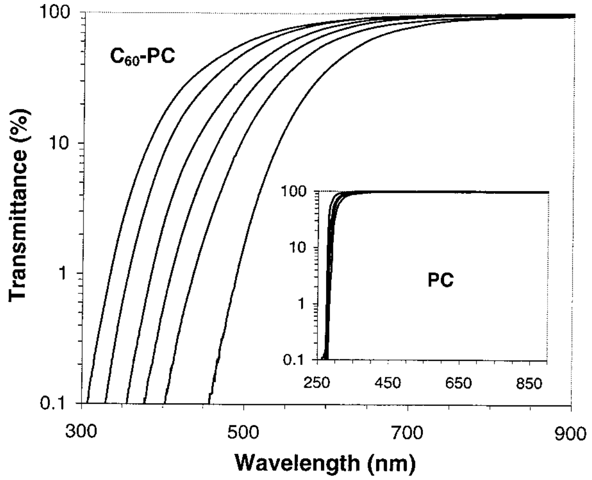

Figure 8. Light transmission spectra of THF solutions of C_{60}—PC (sample from Table 1, no. 4). Concentration (mg/mL; from left to right along the abscissa): 6.3, 9.4, 14.1, 18.8, 28.2, 56.4. Transmission spectra of THF solutions of PC are shown in the inset for comparison: concentration (mg/mL; from left to right), 2.1, 4.2, 8.4, 16.7.

In the course of investigating the optical limiting performance of the C_{60}—PCs, we had to check their linear transmittance by a UV—vis spectrophotometer. Although the electronic transition spectra of the dilute THF solutions of the C_{60}—PCs had some fine structures (cf. Figure 5), their light transmission spectra in the high-concentration region were completely structureless, much like the transmission curves of typical cutoff optical filters. Interestingly, the transmission spectrum of the C_{60}—PC solutions horizontally red-shifted with increasing concentration with little change in shape. A cutoff wavelength (λ_c) might be defined as the wavelength at which the transmittance is 0.1%. Thus, when the concentration (*c*) of the THF solution of a C_{60}—PC (C_{60} content, 1.23 wt %) was 6.3 mg/mL, its λ_c was 306.79 nm (Figure 8). When *c* increased to 56.4 mg/mL, λ_c shifted to 456.51 nm. On the other hand, like other common organic molecules, the starting PC exhibited no such bathochromic spectral shift.

We plotted λ_c against *c* of the THF solutions of the C_{60}—PC (Figure 9A) and found that there was a semilogarithmic relationship between λ_c and *c*:

$$\lambda_c = \alpha \log c + k \qquad (4)$$

where α and *k* are constants. When the C_{60} content of C_{60}—PC increased to 1.46 wt %, the λ_c—*c* line moved up vertically (red-shift at the same concentration; Figure 9B). A further increase in the C_{60} content further red-shifted the λ_c—*c* line, suggesting that the fullerenes attached to the PC chains are responsible for the spectral shift. The λ_c—*c* plot for the THF solutions of pure PC was almost parallel to the abscissa: The concentration change had little effect on the λ_c of the PC solutions. The λ_c for the C_{60}/1,2-dichlorobenzene (DCB) solutions, however, red-shifted with increasing concentration (Figure 9E). The data thus confirm that the novel light transmission phenomenon originates from the C_{60} molecules.

The slope of the λ_c—*c* plot or the α value in eq 4 is a measure of the sensitivity of the spectral shift to concentration. The C_{60}/DCB solutions had an α value of 46.3. Interestingly, the C_{60}/1-chloronaphthalene solutions gave a higher α value (80.8; Figure 9D),

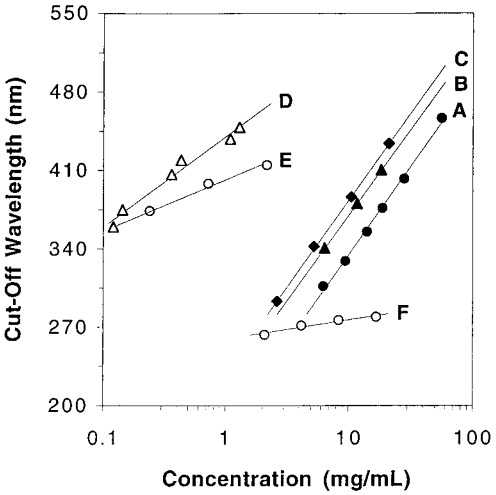

Figure 9. Concentration dependence of the cutoff wavelength of THF solutions of C_{60}−PCs. C_{60} content (wt %): (A) 1.23, (B) 1.46, (C) 2.16. Data for C_{60} solutions in (D) 1-chloro-naphthalene and (E) 1,2-dichlorobenzene and for (F) PC solutions in THF are shown for comparison.

suggesting stronger electronic interaction between the C_{60} cages and the polycyclic rings. The THF solutions of the C_{60}−PCs with different C_{60} contents all gave very high α values (152.9−157.3); in other words, a small change in a narrow concentration range readily shifts λ_c over a wide wavelength range. The pronounced bathochromic effect might have reasons similar to those responsible for the enhanced optical limiting in the C_{60}−PC solutions: (i) the high absorptivity resulting from the chemical modifications of the fullerene molecular structure and (ii) the supramolecular π−π interaction between the electron-accepting C_{60} cages and the electron-rich PC aromatic rings.[11,15] Further studies to understand the exact mechanisms involved in enhancing the optical limiting power and in shifting the light transmission spectra of the C_{60}−PCs are on the way.

Concluding Remarks

In this study, we fullerenated PC, a typical step-growth polymer, using $AlCl_3$ as a catalyst. The $AlCl_3$-catalyzed fullerenation has the following noteworthy features: (i) It is simple, involving only a one-pot experimental procedure; (ii) it is straightforward, involving direct reaction between C_{60} and PC and thus obviating the needs for prefunctionalizing the fullerene and the polymer; (iii) it proceeds in a controlled manner, offering the freedom in fine tuning the extent of fullerenation without generating insoluble products; and (iv) it may have general applicability to a wide range of step-growth polymers because it proves that the aromatic rings with polar functional groups can react with C_{60} in the presence of $AlCl_3$,[5] albeit at somewhat demanding reaction conditions. While the fast fullerenation of polystyrene often yields cross-linked products, the slow fullerenation of PC enables the preparation of soluble C_{60}−PCs.

The attachment of the PC chains to the C_{60} cages has not only improved the fullerene's processibility but also modified its optical properties. The C_{60}−PC solutions effectively limit the strong optical pulses, and their light transmission spectra continuously red-shift with increasing concentration. The high solubility of the C_{60}−PCs enables easy tuning of their optical properties by simply changing their concentration, which, in the case of blocking light of specific wavelengths, can even be accomplished in a predictable manner (cf. eq 4). Since the generation of light with defined spectral characteristics is of fundamental importance and the control of light intensity is crucial to the development of laser-based optical technologies, C_{60}−PCs with the unique wavelength shielding and optical limiting properties may find a wide range of technological applications in optics-related industries.

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