C_{60}-Containing Poly(1-phenyl-1-alkynes): Synthesis, Light Emission, and Optical Limiting[†]

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While polymerizations of 1-phenyl-1-propyne (PP) and 1-phenyl-1-butyne (PB) initiated by WCl_6-Ph_4Sn at room temperature yield small amounts of polymers (0.05−5.3%) with low molecular weights (M_n 8000−15000) and high polydispersity indexes (PDI up to 109), addition of C_{60} into the initiator mixture dramatically boosts its catalytic activity, producing polymers with high M_ns (up to 171 000) and low PDIs (down to 2.2) in high yields (up to 99.5%). The resultant polymers are soluble, stable, and film-forming. GPC, IR, NMR, UV, and XRD analyses reveal that the polymers consist of polyacetylene chains and covalently bound C_{60} cages (up to 9.1 wt %). Whereas photoluminescence of C_{60}-containing polyPPs is faint, C_{60}-containing polyPBs emit strong blue light ($\lambda_{max} = 456$ nm) readily observable with the naked eye under normal laboratory lighting. Compared with the parent C_{60}, both two groups of the fullerene polyacetylenes show better optical limiting performance, and their THF solutions, with higher linear transmittance, attenuate the power of intense 532 nm optical pulses to lower saturation fluence.

Introduction

Since the discovery of the bulk preparation method of gram quantities of C_{60}, vigorous research has been devoted to fullerene chemistry, which has resulted in a wealth of information on the chemical reactions of C_{60}.[1] C_{60} readily reacts with nucleophiles and undergoes all kinds of reactions associated with an electron-deficient cycloolefin. One of the best-known fullerene reactions is the nucleophilic coupling of carbene species with C_{60}, leading to the formation of methanofullerene adducts.

Taking advantage of the olefinic reactivity of C_{60}, in our previous studies, we developed several simple polymer reactions for directly attaching C_{60} cages to macromolecular chains of commercially important plastics such as polycarbonate and poly(vinyl chloride).[2] The alkene chemistry of C_{60} has also been utilized by many research groups in the synthesis of fullerene polymers. Typical examples include the direct copolymerizations of C_{60} with methyl methacrylate,[3,4] styrene,[3b,4,5] 4-vinylbenzoic acid,[6] 2-cyanoethyl acrylate,[7] cyanovinyl acetate,[7] *p*-xylene (or paracyclophane),[8] bis-*o*-quinodimethanes,[9] and bisanthracene ether.[10] Almost all the polymers for hosting the C_{60} cages in the above-mentioned polymer reactions[2] and copolymerizations[2−10] are saturated (or nonconjugated) macromolecules. Incorporation of C_{60} molecules into unsaturated (or conjugated) polymers is of interest from the viewpoints of developing advanced materials with novel molecular architectures. C_{60}-containing conjugated polymers may show unique optical and electronic properties contributing from the fullerene cages and the conjugated macromolecules. Such a possibility, intrigue notwithstanding, has not been well explored. Optical properties of fullerene/conjugated polymer blends have been extensively studied;[11] such blends, however, often suffer from the problems of morphological inhomogeneity and optical nonuniformity.

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Polyacetylenes $-(RC{=}CR')_n-$ are prototypical conjugated polymers. Through molecular engineering endeavors in designing the chemical structures of the pendant groups R and R′ attached to the alternating-double-bond backbone, we have recently succeeded in synthesizing a wide variety of polyacetylenes with novel materials properties such as liquid crystallinity,[12] photo- and electoluminescence,[13] optical activity (chirality),[14] photoconductivity,[12k,15] and solvatochromism.[16] In our previous study on wrapping carbon nanotubes with poly(phenylacetylene) $[-(PhC{=}CH)_n-]$, we found that the poly(phenylacetylene) chains were indelibly attached to the fullerene hemispheres at the ends of the nanotubes.[17] The nature of chemical bonding between the polyacetylene and the fullerene was confirmed by the successful synthesis of C_{60}-containing poly(phenylacetylene)s, in which the buckyballs are covalently incorporated into the conjugated polymer chains.[18] Poly(phenylacetylene) itself is, however, not stable[17,19] and has poor film-forming ability;[20] which significantly limits the scope of practical applications of the C_{60}-containing poly(phenylacetylene)s.

In this work, we extended our efforts to the exploration of the possibility of incorporating fullerene into poly(1-phenyl-1-alkynes) $-[PhC{=}C(C_mH_{2m+1})]_n-$, the poly(phenylacetylene) cousins with excellent chemical stability[19] and mechanical properties.[20] We investigated the polymerizations of the phenylalkynes catalyzed by WCl_6-Ph_4Sn in the presence of C_{60} and found that C_{60} was readily integrated into the poly(phenylalkyne) structure. Delightfully, we also observed that C_{60} remarkably accelerated the W-initiated acetylene polymerizations. The resultant C_{60}-containing poly(1-phenyl-1-propyne)s ($C_{60}-PPPs$) and poly(1-phenyl-1-butyne)s ($C_{60}-PPBs$) show unique optical properties: Both the $C_{60}-PPPs$ and $-PPBs$ limit intense optical power, while the $C_{60}-PPBs$ strongly luminesce upon photoexcitation.

Experimental Section

Materials. C_{60} (99.95% pure) was purchased from MER and kept in the dark before use. The 1-phenyl-1-alkyne monomers, i.e., 1-phenyl-1-propyne (PP; $PhC{\equiv}CCH_3$) and 1-phenyl-1-butyne (PB; $PhC{\equiv}CC_2H_5$), were purchased from Farchan Laboratories, distilled from calcium hydride under reduced pressure, and stored in sealed ampules in a refrigerator. High-purity tungsten(VI) chloride and tetraphenyltin (Aldrich) were used as received. Spectroscopic grade THF and toluene (Aldrich) were predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. All other solvents were purchased from Aldrich and used without further purification.

Instrumentation. Weight- (M_w) and number-average molecular weights (M_n) and polydispersity index (M_w/M_n) were estimated by a Waters 510 gel permeation chromatograph (GPC).[2] IR spectra were measured on a Perkin-Elmer 16 PC spectrophotometer using KBr disks or pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker ARX300 spectrometer using chloroform-*d* as solvent. UV−vis absorption spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer using a 1-cm^2 quartz cell. X-ray diffraction (XRD) patterns were recorded on a Philips PW 1830 powder diffractometer with a graphite monochromator using 1.5406 Å Cu Kα wavelength at room temperature (scanning rate 0.02 °/s; scan range 3−27°). Mass spectra were obtained with the use of a Finnigan TSQ7000 triple quadrupole mass spectrometer operating in a direct-insertion-probe chemical ionization (DCI) mode using methane as reagent gas.

Polymerization. All polymerization reactions and manipulations were carried out under nitrogen using either a vacuum-line system or an inert-atmosphere glovebox (Vacuum Atmosphere MO-20), except for the purification of polymers, which was done in the air. Typical examples of experimental procedures for the polymerizations of the phenylalkynes in the presence of C_{60} are given below.

Polymerization of PP in the Presence of C_{60}. Into a baked 20-mL Schlenk tube under nitrogen at room temperature were added 30 mg of C_{60}, 84 mg of WCl_6, 102 mg of Ph_4Sn, and 2.5 mL of freshly distilled toluene. The catalyst solution was stirred (aged) for 30 min, into which was then injected a monomer solution of PP (0.6 mL) in toluene (2.5 mL). After stirring under nitrogen for 24 h, the reaction was quenched with 5 mL of toluene containing a small amount of methanol, and the diluted reaction mixture was filtered through a cotton filter. The soluble filtrate was added dropwise into 400 mL of methanol under stirring to precipitate the polymer product. The product was redissolved in THF, and the solution was centrifuged at 2000 rpm for 16 min. The supernatant was added dropwise through a cotton filter into hexane (∼300 mL). The dissolution−precipitation process was repeated several times, and the finally isolated precipitant was dried under vacuum at 40 °C to a constant weight. A gray-colored powder was obtained in 56.8% yield; M_n 10 000, M_w/M_n 4.5. The spectroscopic data of the product are given in Figures 2 (IR), 5 (^{1}H NMR), 6 (^{13}C NMR), and 7 (UV). XRD (powder, Cu Kα), 2θ (deg)/d (Å): 10.62/8.32, 17.64/5.02, 20.68/4.29, 21.40/4.13.

Polymerization of PB in the Presence of C_{60}. A mixture of C_{60} (20 mg), WCl_6 (40 mg), and Ph_4Sn (51 mg) in 2.5 mL of toluene was stirred in an oven-dried 20-mL Schlenk tube for 30 min at room temperature under nitrogen. A toluene (2.5 mL) solution of purified PB (0.5 mL) was then injected into the aged catalyst solution. After polymerization at room temperature for 24 h, the polymer product was isolated and purified by the procedure detailed above. A gray powder was obtained in 85.1% yield; M_n 170 000; M_w/M_n 2.2. IR (KBr), ν (cm^{-1}): 3050 (m), 2964 (m), 2932 (m), 2872 (m), 1596 (m), 1490 (s), 1440 (s), 1370 (m), 1322 (w), 1274 (w), 1214 (w), 1154 (w),

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Table 1. Polymerizations of 1-Phenyl-1-Propyne (PP) in the Absence and Presence of C_{60}[a]

no.	PP (mL)	C_{60} (mg)	C_{60}/PP (wt %)	WCl_6 (mg)	Ph_4Sn (mg)	yield (wt %)	$M_n/10^3$ [b]	M_w/M_n [b]	C_{60} content (wt %)[c]
1	0.50	0	0	20	17	0.5	8	109.0	0
2	0.50	6	1.3	22	27	77.3	17	6.3	1.3
3	0.55	12	2.4	82	100	75.0	9	15.7	3.8
4	0.56	21	4.0	86	99	80.3	12	35.4	6.2
5	0.60	30	5.4	84	102	56.8	10	4.5	9.1

[a] Carried out in toluene (5 mL) in the absence (no. 1) and presence (nos. 2−5) of C_{60} in an atmosphere of dry nitrogen at room temperature for 24 h. Aging time of the catalyst system: 30 min. [b] Estimated by GPC in THF on the basis of a polystyrene calibration. [c] Estimated by IR analysis using eq 1.

1072 (m), 1032 (m), 910 (w), 842 (w), 762 (s), 696 (s), 526 (w). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.85−5.14, 3.30−0.15. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 141.4, 137.9, 131.7, 131.1, 129.0, 127.1, 26.7, 12.1. UV (THF, 0.013 mg/mL), λ_{max} (nm): 232, 324. XRD (powder, Cu Kα), 2θ (deg)/d (Å): 9.38/9.42, 20.36/4.36, 21.62/4.11.

Determination of C_{60} Content. IR analysis was used to estimate the C_{60} contents of the polymers. To establish a calibration curve, a series of C_{60}/poly(1-phenyl-1-alkyne) mixtures with known amounts of C_{60} were prepared. The pure poly(1-phenyl-1-alkyne) samples were prepared by the acetylene polymerizations initiated by $TaCl_5$−Ph_4Sn at 80 °C according to published procedures.[21] To ensure intimate mixing, poly(1-phenyl-1-alkyne) and C_{60} were first dissolved in a solvent, cast into a thin film, and then thoroughly ground with KBr powders in a smooth agate mortar. The out-of-plane ring C═C bending vibration of polyacetylenes with phenyl pendants occurs at 696 cm^{-1}, and C_{60} exhibits a "robust" absorption band at 526 cm^{-1}, which often survives the functionalization at the fullerene cage and whose intensity is not much affected by the chemical environment.[2,4,5] The phenyl band at 696 cm^{-1} was used as the internal standard, and the ratios of the intensities of the bands at 526 and 696 cm^{-1} (I_{526}/I_{696}) were plotted against the C_{60} contents. The plot gave a calibration line (vide post; cf., Figure 3) observing the following linear relationship:

$$C_{60} \text{ content (wt \%)} = 65.4\ I_{526}/I_{696} - 1.3 \qquad (1)$$

The peak intensities were determined by the well-established tangential baseline method.[22]

Reaction of C_{60} with WCl_6 and/or Ph_4Sn. C_{60} was allowed to react with WCl_6 and/or Ph_4Sn in toluene at room temperature under nitrogen. In a typical run for the reaction of C_{60}, WCl_6, and Ph_4Sn, 1.5 mg of C_{60}, 2.7 mg of WCl_6, and 3.2 mg of Ph_4Sn were admixed in an oven-dried 20-mL Schlenk tube. Freshly distilled toluene (5 mL) was then added to the tube, and the resultant solution was stirred for 24 h. The reaction mixture was directly injected into the MS spectrometer for analysis. Products with a general molecular formula of $Ar_mC_{60}H_m$ (m = 1−4) were identified. MS (DCI, CH_4): m/z 720.8 (C_{60} + H^+, calcd 721.0), 749.1 (C_{60} + $C_2H_5^+$, calcd 749.0), 813.0 ($PhC_{60}H$ + CH_3^+ or $PhCH_2C_{60}H$ + H^+, calcd 813.1), 903.5 ($Ph_2C_{60}H_2$ + $C_2H_3^+$, calcd 903.1), 995.6 ($Ph_3C_{60}H_3$ + $C_3H_5^+$, calcd 995.2), 1073.4 ($Ph_4C_{60}H_4$ + $C_3H_5^+$, calcd 1073.2), 1087.6 ($Ph_4C_{60}H_4$ + $C_4H_7^+$, calcd 1087.2).

Optical Measurements. Solutions for light-emitting and optical-limiting measurements were prepared immediately prior to use by dissolving accurately weighed amounts of polymers in freshly distilled and degassed spectroscopic grade THF or toluene using volumetric flasks. Photoluminescence spectra were recorded at room temperature in a quartz cell on a SLM Aminco JD-490 spectrofluorometer. The excitation wavelength was set at 320 nm, where both the poly(phenylalkynes) and C_{60} absorb. Optical-limiting experiments were performed at 532 nm, using 8-ns optical pulses generated from a frequency-doubled Q-switched Nd:YAG laser (Quanta Ray GCR-3) operating in a near-Gaussion transverse mode with a repetition rate of 10 Hz.[2] The pulsed laser beam was focused onto a 1-cm^2 quartz cell filled with a solution. 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.

Results and Discussion

Polymerization. In general, W-based catalysts can effectively polymerize monosubstituted (terminal) acetylenes (HC≡CR) but not disubstituted (internal) ones (RC≡CR′).[23] It was thus not a big surprise to us when we isolated only a trace amount of polymer (0.5%) from our attempted polymerization of PP initiated by WCl_6−Ph_4Sn (Table 1, no. 1). However, when a small amount of C_{60} (6 mg) is added into the W catalyst system, the polymer yield dramatically increases to 77.3%. To make sure this was not an experimental error, we added different amounts of C_{60} into the polymerization system, and in all cases, high molecular weight polymers were isolated in high yields (Table 1, nos. 2−5).

While the polymer obtained from the polymerization initiated by WCl_6−Ph_4Sn alone (in the absence of C_{60}) shows multiple GPC peaks over a wide range of molecular weights, the polymers produced in the presence of C_{60} exhibit only two peaks in a narrower molecular weight region (Figure 1). Thus, C_{60} is acting as a cocatalyst in the PP polymerization: Its addition to the W catalyst system does not only boost the yield of the polymer but also narrows its molecular weight distribution.

While the pure poly(1-phenyl-1-propyne) (PPP) obtained in the absence of C_{60} is white, the polymers isolated from the WCl_6−Ph_4Sn−C_{60} catalyst system are colored. To check whether the coloration is due to the C_{60} aggregates physically trapped in the polymer matrix, we dissolved the polymers in THF, a good solvent of PPP[21] but a poor solvent of C_{60}.[24] The resultant THF solutions were then centrifuged and filtered. The homogeneous and transparent filtrate was added dropwise into hexane, a nonsolvent of PPP[21] but a solvent of C_{60},[24] and the polymer precipitate was collected by filtration with the use of gooch crucibles. The dissolu-

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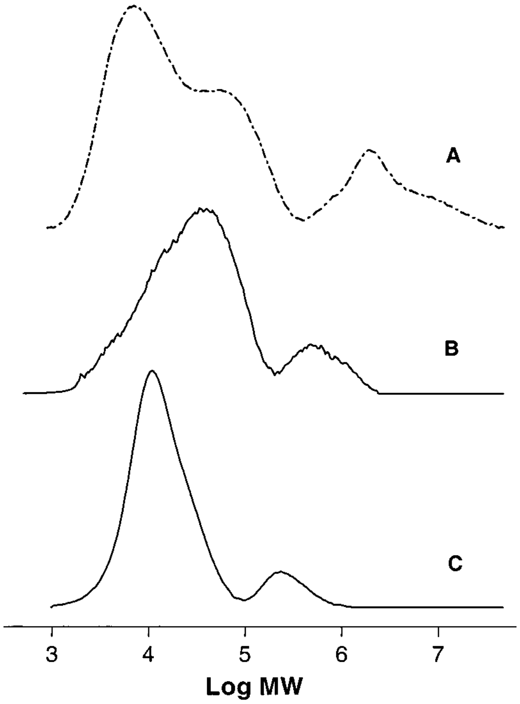

Figure 1. GPC traces of the products of the polymerizations of 1-phenyl-1-propyne initiated by WCl_6-Ph_4Sn in the (A) absence and (B, C) presence of C_{60} [samples from Table 1, nos. 1 (A), 2 (B), and 5 (C)].

tion–filtration process should remove the insoluble C_{60} particles from the THF solutions of the polymers and the following precipitation–filtration process should remove the C_{60} molecules dissolved in hexane from the polymer sediment. We repeated the dissolution–centrifugation–filtration–precipitation–filtration processes more than three times but the polymer products we finally isolated were still colored. The C_{60} molecules thus must have been indelibly attached to the polymer chains.

We further conducted a physical blending experiment. We stirred a mixture of C_{60} and PPP in toluene under nitrogen at room temperature for 24 h. The PPP was indeed tinged but addition of the mixture into THF readily separated the PPP matrix and the C_{60} particles, with the polymer staying in solution but the C_{60} particles precipitating out from the THF solution. This control experiment further reduces the likelihood of physical trapping of C_{60} in the products isolated from the polymerization reactions and suggests that the C_{60} cages have been chemically bound to the PPP chains.

Figure 2 shows the IR spectrum of a C_{60}-containing PPP along with the spectra of the parent C_{60} and PPP. The IR spectrum of the C_{60}–PPP is similar to that of PPP, with a few additional new bands at 670, 578, and 526 cm^{-1}. By comparison with the spectrum of C_{60}, these new bands are obviously from the absorption of the C_{60} moieties in the polymer. The band at 526 cm^{-1} has often served as a diagnostic absorption for the identification of C_{60} incorporation into macromolecular chains.[2,4,5,7] Indeed, all the C_{60}–PPPs prepared in this study exhibit absorption bands at 526 cm^{-1}, whose intensities vary with the feed ratios of C_{60} in the polymerization reactions. This suggests that the band at 526 cm^{-1} can be further utilized to estimate the C_{60} contents of the polymers. We thus prepared a set of C_{60}/PPP mixtures

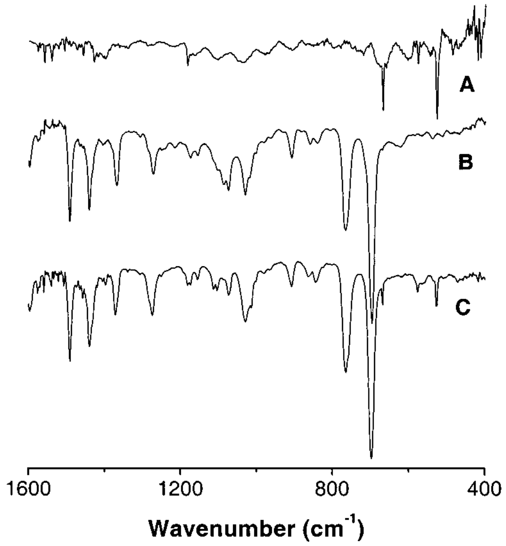

Figure 2. IR spectra of (A) C_{60}, (B) poly(1-phenyl-1-propyne), and (C) C_{60}-containing poly(1-phenyl-1-propyne) (sample from Table 1, no. 5).

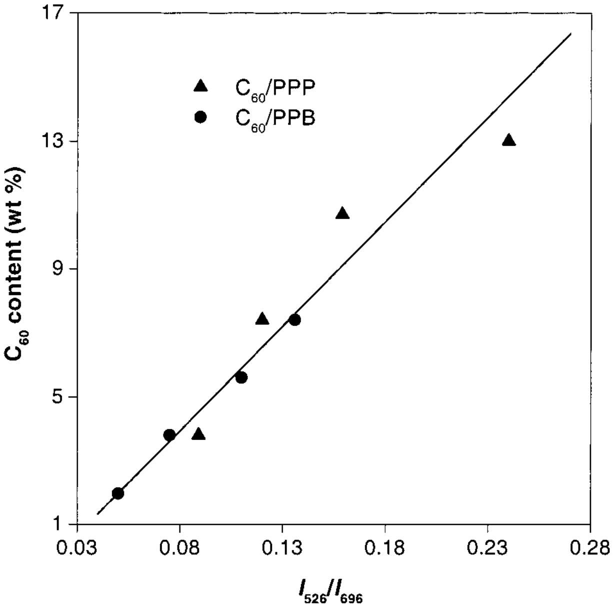

Figure 3. Calibration curve for determining C_{60} contents of C_{60}-containing poly(1-phenyl-1-alkynes) using the intensity ratios of the absorption bands of C_{60} at 526 cm^{-1} and phenyl at 696 cm^{-1}.

with known amounts of C_{60} and then measured their IR spectra. Using the strong absorption band of the phenyl rings in the PPP chain at 696 cm^{-1} as an internal standard, we plotted the I_{526}/I_{696} ratios against the C_{60} contents and obtained a calibration line observing eq 1 (Figure 3).

We then estimated the C_{60} contents of the C_{60}–PPPs using their IR data and eq 1. As shown in Table 1, when the feed ratio of C_{60}/PP in the monomer solution is 1.3%, the C_{60} content of the isolated polymer is coincidentally also 1.3%. When the C_{60}/PP feed ratio increases, the C_{60} content of the polymer also increases. In other words, the amount of C_{60} incorporated into PPP can be easily manipulated by simply changing the monomer feed ratio. Thus, when the C_{60}/PP ratio is increased to 5.4%, the C_{60} content of the polymer increases to a value as high as 9.1% (Table 1, no.5).

Table 2. Polymerizations of 1-Phenyl-1-Butyne (PB) in the Absence and Presence of C_{60}[a]

no.	C_{60}/PB feed ratio[b] (wt %)	yield (wt %)	$M_n/10^3$ [c]	M_w/M_n [c]	C_{60} content (wt %)[d]
1	0	5.3[e]	15	7.0	0
2	0.9	83.1	76	2.2	2.8
3	4.4	85.1	170	2.2	3.9
4	5.7	87.9	171	3.1	7.9

[a] Catalyzed by WCl_6 (40 mg) and Ph_4Sn (51 mg) in toluene (5 mL) in the absence (no. 1) and presence (nos. 2−4) of C_{60} under nitrogen at room temperature for 24 h. Aging time of the catalyst system: 30 min. [b] PB: 0.5 mL. [c] Estimated by GPC in THF on the basis of a polystyrene calibration. [d] Estimated by IR analysis using eq 1. [e] To double confirm the ineffectiveness of the WCl_6−Ph_4Sn catalyst system, the reaction was repeated under identical conditions and the polymer yield was found to be reproducibly low (2.1 wt %).

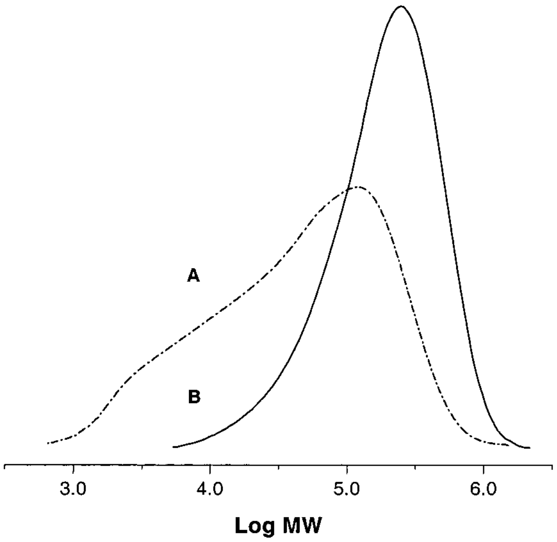

Figure 4. GPC traces of the products of the polymerizations of 1-phenyl-1-butyne initiated by WCl_6−Ph_4Sn in the (A) absence and (B) presence of C_{60} [samples from Table 2, nos. 1 (A) and 4 (B)].

We further investigated polymerization reactions of another phenylalkyne, PB, which possesses a longer alkyl group. In the absence of C_{60}, the W-catalyzed polymerization at room temperature produces little amount (5.3%) of poly(1-phenyl-1-butyne) (PPB; Table 2, no.1). We repeated the polymerization experiment and found that the polymer yield was reproducibly low (2.1%), confirming that WCl_6−Ph_4Sn is indeed an ineffective catalyst for the PB polymerization at room temperature. When C_{60} is added to the W catalyst system, the polymer yield again strikingly increases. The purified polymer products are again colored and show the characteristic IR absorption bands of C_{60} and PPB, proving that the polymer products are C_{60}−PPBs.

The polymerization of PB in the presence of C_{60} is, however, much “cleaner” than that of its C_{60}/PP counterpart. While the polymers obtained from the C_{60}/PP polymerizations show bimodal GPC chromatograms, the C_{60}−PPBs exhibit unimodal GPC peaks. It is clear from Figure 4 that, compared to the parent PPB, the C_{60}−PPB has higher molecular weights but a narrower molecular weight distribution. The addition of C_{60} to the polymerization reaction has depressed the formation of the oligomeric species. The lower viscosity and hence higher mobility of the shorter chains[25] confers on the oligomers higher chances to combine with the C_{60} cages. One C_{60} cage may link several oligomers together, effectively consuming the oligomeric species and hence shifting the GPC curve to the high molecular weight region. When the C_{60}/PB feed ratio increases, both the molecular weight and the C_{60} content of the C_{60}−PPB increases (Table 2, nos. 2−4). Remarkably, although the C_{60}−PPB prepared using a C_{60}/PB feed ratio of 5.7% has high M_n (171000) and C_{60} content (7.9%), the polymer is completely soluble in common organic solvents such as THF, toluene, and chloroform. This suggests that no cross-linking reactions have occurred in the polymerization system.

Table 3. Effect of Aging on the Polymerizations of 1-Phenyl-1-Butyne (PB) in the Presence of C_{60}[a]

no.	C_{60}/PB feed ratio[b] (wt %)	aging time (min)	polymer yield (wt %)	$M_n/10^3$ [c]	M_w/M_n [c]
1	5.7	1	16.5	26	5.4
2	5.7	15	48.2	48	3.3
3	5.7	30	87.9	171	3.1
4	5.7	60	61.8	51	2.5
5	2.5	15	99.5	43	3.2

[a] Carried out under nitrogen in toluene (5 mL) at room temperature for 24 h. Initial amount of PB: 0.5 mL. [b] Estimated by GPC in THF on the basis of a polystyrene calibration.

To learn more about the polymerization behavior, we carried out some more detailed investigations. We first checked the cocatalyst effects on the acetylene polymerizations initiated by the WCl_6−Ph_4Sn−C_{60} system. Neither WCl_6−Ph_4Sn nor WCl_6−C_{60} can effect the PP polymerization. Similar results are obtained in the PB polymerization. It thus becomes clear that both the cocatalysts, namely, C_{60} and Ph_4Sn, are indispensable components of the W-based catalyst system.

When C_{60} is admixed with WCl_6−Ph_4Sn in toluene, the color of the solution gradually changes during the aging process from dark blue to dark green and then to brown. The color change suggests that C_{60} has undergone some chemical reactions and/or experienced some coordinate interaction with the WCl_6−Ph_4Sn mixture. If this is the case, the aging time of the catalyst solution should affect the polymerization reaction. Indeed, as can be seen from Table 3, the aging process does make a difference. When the catalyst solution is aged for a short time of 1 min, the polymer yield is as low as 16.5% and the PDI is as high as 5.4. Increasing the aging time up to 30 min (while keeping other conditions identical) monotonically increases the polymer yield and decreases the PDI value (Table 3, nos. 2 and 3). When the aging time is further increased to 60 min, the yield somewhat drops, whereas the PDI further decreases. There seems to exist a window of optimal aging time, and in this study, the aging time of 30 min is adopted for most of the polymerization reactions. The “optimal” aging time can be shorten by reducing the feed amount of C_{60}: only 15-min aging is required to achieve a 99.5% polymer yield when the C_{60}/PB feed ratio is decreased to 2.5% (Table 3, no. 5).

Characterization. The excellent solubility of the C_{60}-containing polyacetylenes enables characterization of their molecular structures by solution spectroscopic

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(25) (a) Stevens, M. P. *Polymer Chemistry, an Introduction*, 3rd ed.; Oxford University Oress: New York, 1999.

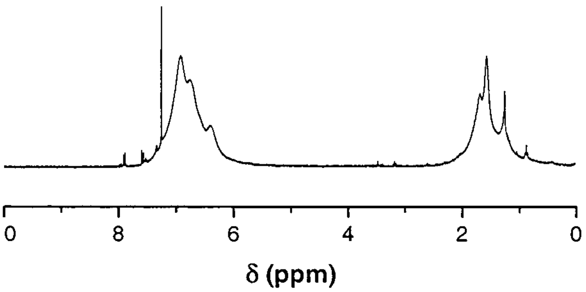

Figure 5. ^{1}H NMR spectrum of chloroform-*d* solution of a C_{60}-containing poly(1-phenyl-1-propyne) (sample from Table 1, no. 5).

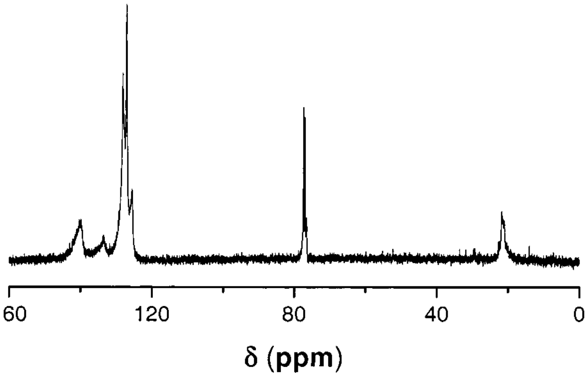

Figure 6. ^{13}C NMR spectra of chloroform-*d* solution of a C_{60}-containing poly(1-phenyl-1-propyne) (sample from Table 1, no. 5).

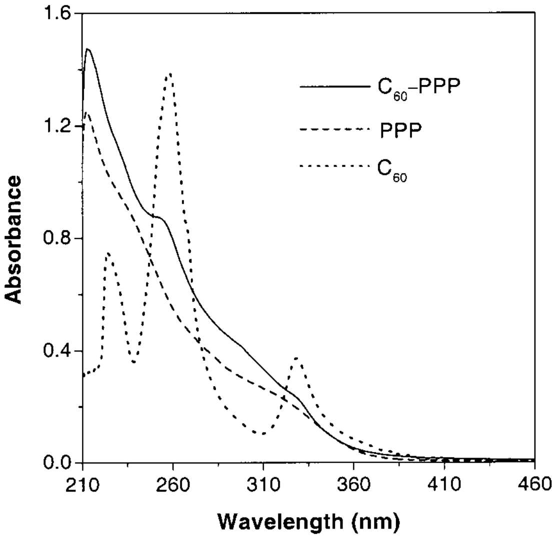

Figure 7. UV spectrum of a C_{60}-containing poly(1-phenyl-1-propyne) (sample from Table 1, no. 5) in THF (concentration: 0.013 mg/mL). The spectra of poly(1-phenyl-1-propyne) in THF (0.013 mg/mL) and C_{60} in hexane (0.011 mg/mL) are also shown for comparison.

methods. Figure 5 shows ^{1}H NMR spectrum of a chloroform solution of a C_{60}−PPP. The polymer exhibits two groups of peaks in the chemical shift regions of δ 7.6−5.7 and δ 2.4−0.2. The three broad peaks in the downfield are assignable to the aromatic protons of the pendant phenyl rings of PPP, while those in the upfield are attributable to the methyl protons. Olah et al.[26] have found that the fullerenyl protons in their polyarene-fullerenes $Ar_mC_{60}H_m$ (m up to 12) display a broad peak centered at δ 4.5. Huang and co-workers[27] have observed four broad peaks in δ 5.8−4.0 for the fullerenyl protons in their oligo(4,4′-biphenylenefullerenylene) $-[(Biph)_mC_{60}H_m]_n-$. The C_{60}−PPP, however, does not show any peak in this chemical shift region at all. The lack of the fullerenyl proton suggests that the PPP chains are not linked to the C_{60} cages through an anionic mode followed by H^+ quenching[1] but probably via a carbene mechanism that leads to the formation of methanofullerenes.

Figure 6 shows ^{13}C NMR spectrum of a C_{60}−PPP solution. All the peaks are associated with the PPP structure [δ 140.5 (Ph*C*=), 133.6 (Me*C*=), 139.90 (quaternary carbon of Ph), 128.1 (*ortho* carbon of Ph), 127.2 (*meta* carbon of Ph), 125.6 (*para* carbon of Ph), and 22.8 (Me)]. There are no clearly observable peaks originating from the resonance of the C_{60} moieties in the polymer. This may be due to the low sensitivity of the carbon atoms of fullerene caused by the loss of the 60-fold degeneracy of the original C_{60} cage once it is chemically attached to the PPP chains. An important information provided by the NMR spectrum is that there is no any peak at δ ~143, where an intact C_{60} cage with the I_h symmetry should strongly resonate. This once again confirms that the C_{60} cages are not physically trapped in the PPP matrix but are covalently linked to the PPP chains.

Figure 7 shows the electronic absorption spectra of the C_{60}−PPP and its parents C_{60} and PPP. While the pure PPP exhibits a weak absorption shoulder at 229 nm, the C_{60}−PPP displays a clear hump at 256 nm, which, by comparison with the spectrum of pure C_{60}, is evidently due to the absorption of the fullerene moiety in the polymer. C_{60} absorbs at 328 nm. This absorption peak is known to be sensitive to chemical reactions: its intensity weakens upon chemical modification to the molecular structure of the C_{60} cage.[2,5,28] The C_{60}−PPP shows a weak but readily discernible absorption shoulder at 330 nm, confirming that the molecular structure of C_{60} has been modified by the polymerization reaction. The THF solutions of physical mixtures of C_{60} and PPP scatter visible light, giving a flat line parallel to and well above the wavelength abscissa from ~400 nm. The THF solution of the C_{60}−PPP is homogeneous and transparent and does not show such a scattering line in the visible spectral region. The C_{60} cages thus must have been chemically bound to the PPP chains in a uniform fashion.

Fullerene molecules have a strong tendency to aggregate in the solid state and also in the solution phase.[2,4,29] In the solid state, C_{60} cages regularly pack in their crystal lattice, giving sharp and intense XRD reflection peaks at Bragg angles of 10.62°, 17.64°, 20.68°, and 21.40° (with corresponding *d* spacing values

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(26) Olah, G. A.; Busci, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1991**, *113*, 9387.

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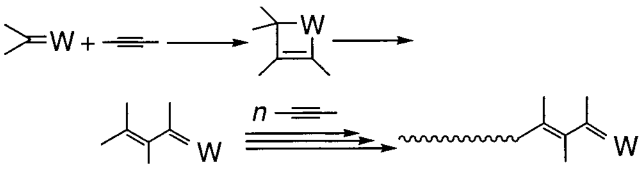
(29) (a) Matin, T. P.; Naher, U.; Schaber, H.; Zimmermann, U.; *Phys. Rev. Lett.* **1993**, *70*, 3079. (b) Beeby, A.; Eastoe, J.; Heenan, R. K. *Chem. Commun.* **1994**, 173. (c) Sun, Y.-P.; Bunker, C. E. *Nature* **1993**, *365*, 398. (d) Ying, Q.; Marecek, J.; Chu, B. *Chem. Phys. Lett.* **1994**, *219*, 214. (e) Bensasson, R. V.; Bienvenue, E.; Dellinger, M.; Leach, S.; Seta, P. *J. Phys. Chem.* **1994**, *98*, 3492. (f) Brettreich, M.; Hirsch, A.; *Tetrahedron Lett.* **1998**, *39*, 2731.

Scheme 1



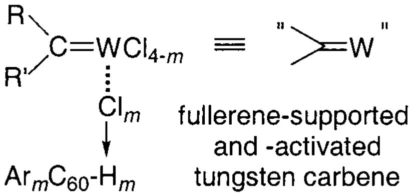
of 8.10, 5.00, 4.26, and 4.07 Å). PPP is, however, an amorphous polymer, displaying two diffuse halos centered at 2θ angles of ~10.8° and ~20.1°. When the C_{60} cages are attached to the PPP chains, hardly any sharp Bragg reflections can be observed. Clearly, the PPP chains wrapping around the C_{60} cages and the structural modifications to the C_{60} molecules by the polymerization reaction have prevented the buckyballs from packing well and obstructed the growth of their crystals.[30]

Mechanism. W-catalyzed acetylene polymerizations are generally believed to propagate via a tungstacarbene-mediated metathesis mechanism (Scheme 1).[23,31] The addition of a molecule of acetylene to the tungsten carbene species gives a tungstacyclobutene that opens to bring about a complex with a new tungsten–carbon double bond. The ring-forming and -opening processes repeat, knitting together the acetylene monomers into polymer chains through the successive metathesis reactions. When C_{60} is added into the WCl_6–Ph_4Sn mixture, the tungsten carbene species may experience coordinate interactions and undergo chemical reactions with the fullerene molecules; the former may enhance the activity of the W catalyst and the latter may incorporate the C_{60} cages into the polyacetylene structure.

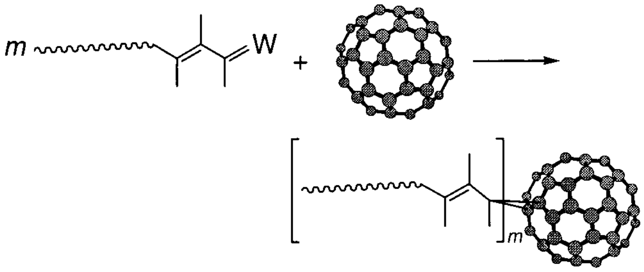
In an effort to understand how the tungsten carbene species are activated by the fullerene molecules, we conducted a control experiment, in which WCl_6, Ph_4Sn, and C_{60} are allowed to react in the absence of the phenylalkyne monomers. MS analysis of the reaction products gives peaks of the molecular ions of $Ar_mC_{60}H_m$ ($m = 1-4$; see Experimental Section for detailed peak assignments). Thus, the reaction produces a mixture of arylfullerenes, although the yields of the higher adducts are very low, being only ~1% when $m = 4$. The phenylfullerenes may be the products of nucleophilic addition of Ph_4Sn to C_{60} (eq 2). To check this hypothesis, we conducted another control experiment, in which Ph_4Sn and C_{60} were allowed to react (in the absence of C_{60}) under identical conditions. The control reaction gives all the MS peaks associated with $Ph_mC_{60}H_m$ ($m = 1-4$), confirming that Ph_4Sn has indeed undergone the nucleophilic addition to the fullerene. The tolylfullerene $PhCH_2C_{60}H$ may be produced by the reaction of benzyl radical of toluene with C_{60} followed by hydrogen abstraction.

$$Ph_4Sn + C_{60} \rightarrow Ph_mC_{60}H_m \quad (m = 1-4) \qquad (2)$$

Chart 1



Scheme 2



In metathesis reactions, acidic cocatalysts or supports are often used to increase the activity of W-based catalysts.[31,32] $W(\equiv CCMe_3)(OCMe_3)_3$, for example, becomes an active metathesis catalyst only after it has been treated by an acidic SiO_2 support.[33] Fagan et al. have checked pK_a of $C_{60}H_2$ and found that the fulleroid is one of the strongest acids known, composed purely of carbon and hydrogen atoms.[34] It has been well-documented that organotin cocatalysts can convert WCl_6 to tungsten carbene complexes of general structure $RR'C{=}WCl_4$.[31,32,35] Such carbenoid species are, however, poor initiators for the metathesis polymerizations of internal acetylenes.[23] The acidic arylfullerenes may act as nanodimension supports to activate the tungsten carbene complexes by pulling the chlorine atom(s) away from the metal core (Chart 1). This facilitates the attack of the acetylene monomers to the active center, thus effecting the phenylalkyne polymerizations.

The next question is how the C_{60} cages are incorporated into the polyacetylene structure. As discussed in the Introduction section, addition of carbene species to C_{60} is one of the most extensively studied fullerene reactions and has become a versatile tool for the synthesis of fullerene adducts with methanofullerene scaffolds.[1] For example, Merlic and Bendorf synthesized their functional methanofullerene by the cyclopropanation reaction between C_{60} and a transition metal carbene complex.[36] In our system, the tungsten carbene species at the ends of the growing polyacetylene chains may also undergo the same cyclopropanation reaction with C_{60}, giving polyacetylene-functionalized methanofullerenes (Scheme 2). In the synthesis of C_{60}-containing polymers, the formation of insoluble gels induced by multiple reactions of C_{60} with chain-propagation species has often been a problem.[1,5,26,28] But in the mechanism depicted

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[32] (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446. (b) Schrock, R. P. *Pure Appl. Chem.* **1994**, *66*, 1447. (c) Breslow, D. S. *Prog. Polym. Sci.* **1993**, 1141. (d) Katz, T. J. *Adv. Organomet. Chem.* **1997**, *16*, 283.

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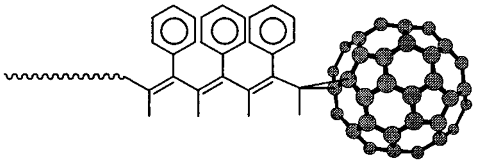
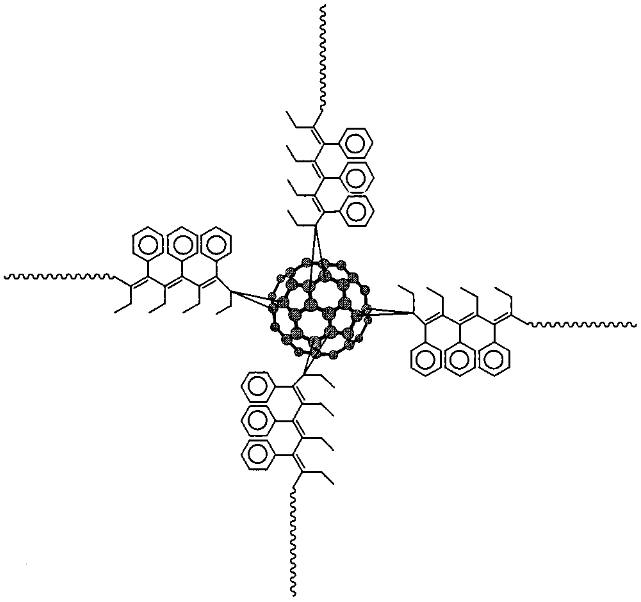
Chart 2



C_{60}–PPP

Chart 3



C_{60}–PPB

in Scheme 2, even when C_{60} undergoes multiple cyclopropanation reactions, it will not produce any cross-linking products, accounting for the experimentally observed excellent solubility of the C_{60}-containing polyacetylenes.

The linkage of the polyacetylene chains by the C_{60} cage should increase the molecular weights of the polymers; in other words, the average values of m of the C_{60}-polyacetylene adducts shown in Scheme 2 can be evaluated by molecular weight changes of the polymer products. From the M_n data listed in Table 1, it is estimated that only one or at most two PPP chains are bound to one C_{60} cage on the average. On the other hand, the molecular weights of C_{60}–PPBs are much higher than that of the pure PPB, suggesting multiple additions of the PPB chains to one C_{60} cage. The schematic presentation of the molecular structures of a C_{60}–PPP with $m = 1$ and a C_{60}–PPB with $m = 4$ are given in Charts 2 and 3, respectively. The different addition numbers in the C_{60}–PPP and –PPB systems are also suggested by the dramatically different light emitting properties of the polymers, which is to be detailed in the following section.

Light Emission. Radiative transitions of C_{60} are exceedingly slow and its intersystem crossing from the excited singlet to the triplet state is very fast and efficient (with the triplet yield close to unity).[37] Monoadducts of C_{60} show photophysical properties similar to those of the parent C_{60}, emitting very weak fluorescence with reported quantum yields on the order of 10^{-4}.[38]

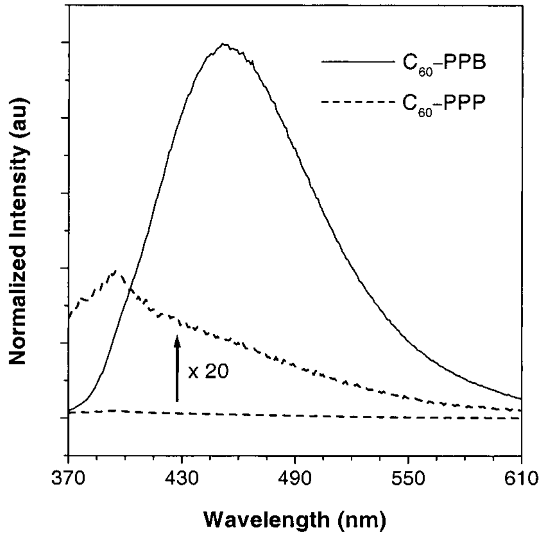


Figure 8. Emission spectra of THF solutions of C_{60}-containing poly(1-phenyl-1-propyne) (C_{60} content: 7.4 wt %; dotted line) and poly(1-phenyl-1-butyne) (C_{60} content: 7.9 wt %; solid line). Concentration: 0.017 mg/mL. Excitation wavelength: 320 nm. The weak signals from the C_{60}–PPP solution are magnified 20 times to show the fine structure of the spectrum.

When a solution of a C_{60}–PPP is excited at 320 nm, it gives practically no fluorescence signals (Figure 8). From the 20-fold enlarged photoluminescence spectrum, the faint light emitted by the polymer is found to be peaked at ~393 nm.

Surprisingly, however, when a solution of a C_{60}–PPB is photoexcited, the polymer emits intense blue light readily observable by the naked eye under normal room illumination conditions. The fluorescence from the C_{60}–PPB is ~50 times stronger than that from its C_{60}–PPP cousin under comparable conditions. This observation is unexpected and the phenomenon is atypical of C_{60} and its derivatives, because the photogenerated electrons in the polymer chains may flow to the C_{60} cages via photoinduced charge-transfer process,[39] effectively quenching the fluorescence of the polymer. We therefore repeatedly measured the photoluminescence of the polymer but found that the unusual phenomenon was experimentally reproducible.

To double-check the reproducibility, we further measured fluorescence spectra of C_{60}–PPBs with different C_{60} contents. As shown in Figure 9, all the C_{60}–PPBs are highly luminescent. The fluorescence intensities of the C_{60}–PPBs are ~1.5-fold higher than that of the pure PPB; that is, instead of quenching, the fullerene molecules actually enhance luminescence of the polymers.

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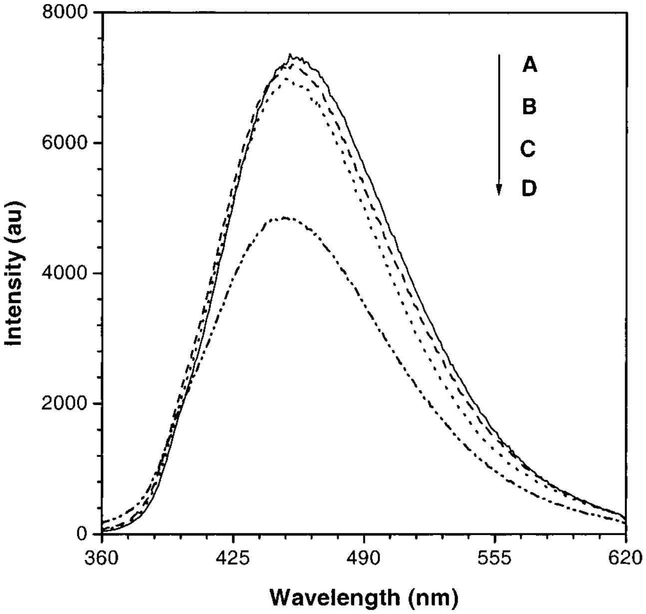

Figure 9. Emission spectra of THF solutions of C_{60}-containing poly(1-phenyl-1-butyne)s excited at 320 nm. C_{60} content (wt %): (A) 2.6, (B) 3.9, (C) 7.9. Concentration (mg/mL): (A) 0.012, (B) 0.017, (C) 0.017. The spectrum of a THF solution of pure poly(1-phenyl-1-butyne) with a concentration of 0.016 mg/mL is shown in (D) for comparison.

Darwish et al.[40] have found that their multiphenylated C_{60} is luminescent, and Schick et al.[41] and Hutchison et al.[42] have recently reported that their hexapyrrolidine derivatives of C_{60} emit bright visible light. As discussed above, the C_{60}−PPPs are mono- or bis-adducts of C_{60} but the C_{60}−PPBs are multiple adducts. The one or two PPP chains attached to one C_{60} cage may not alter the transition energies of the fullerene to a significant extent, and the C_{60}−PPPs thus still largely retain the characteristic photoluminescence properties of the parent C_{60}, exhibiting practically no fluorescence. The multiple PPB chains attached to the C_{60} cages will, however, largely perturb the electronic structures of the fullerene. Thus, the C_{60}−PPBs, like the multiple phenylated and hexapyrrolidine adducts,[40−42] belong to the rare group of C_{60} derivatives that emit strong visible light.

Optical Limiting. Optical limiters are nonlinear optical materials that transmit light of normal intensity but attenuate light of high power.[2,43] The rapid advancements in the laser-based technologies and the growing enthusiasm in the Space exploration have motivated intensive research efforts in the development of new optical limiting materials with better performance characteristics. C_{60} is a passive optical limiter operating in a reverse saturable absorption mode because its excited-state absorption cross section is larger than its ground-state absorption cross section.[44] However, the low sensitivity of C_{60} to the technologically important long wavelength radiation due to its poor solubility in common solvents and poor miscibility with other materials has been an obstacle in finding practical applications for C_{60} as an optical limiter.

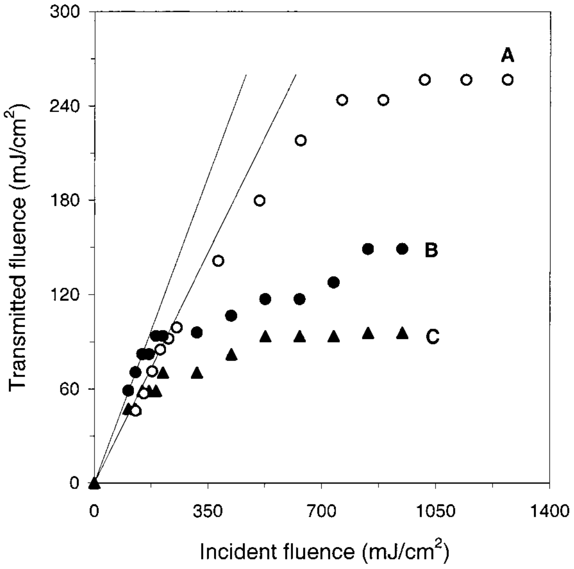

Figure 10. Optical limiting responses to 8-ns, 532-nm optical pulses, of (A) a toluene solution of C_{60} and (B, C) THF solutions of a C_{60}-containing poly(1-phenyl-1-propyne) (sample from Table 1, no. 5); concentration (mg/mL)/linear transmission (%): (A) 0.16/43, (B) 6.00/56, (C) 9.53/43.

When C_{60} cages are wrapped in polymer chains, the soluble macromolecules can drag a large amount of the buckyballs into solvent, enabling the preparation of polymer solutions with high fullerene concentrations.[17,45] The excellent solubility of C_{60}−PPPs enables easy preparation of concentrated solutions. Interestingly, a THF solution of C_{60}−PPP with a higher fullerene concentration shows a higher linear transmittance ($T = 56\%$; Figure 10B) to a pulsed laser beam of 532 nm than does a toluene solution of C_{60} with a lower concentration ($T = 43\%$; Figure 10A). It is known that C_{60} forms aggregates in aromatic solvents (benzene, toluene, etc.).[29,46] Laser-pulse irradiation to C_{60} solutions has also been found to cause thermally induced scattering.[47] As discussed above, the C_{60}−PPP molecules cannot pack well even in the solid state, and it is highly unlikely that the buckyballs will pack better in a solution. The C_{60}−PPP may well be dissolved in the solvent at the molecular level because the PPP chains wrapping around the C_{60} cages effectively prevent the buckyballs from clustering together in the solution. The C_{60}−PPP solution thus may be free of the aggregation- and heat-induced scattering, accounting for its high linear transmittance to the pulsed laser beam.

As shown in Figure 10B, when the intensity of the laser pulses increases to ~150 mJ/cm^2, the fluence

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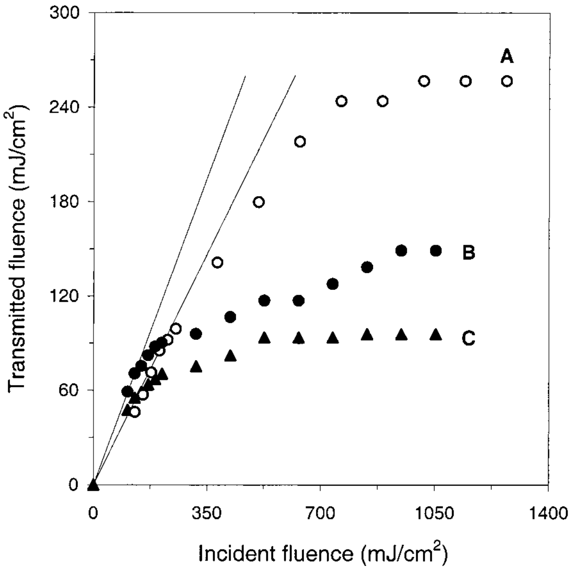

Figure 11. Optical limiting responses to 8-ns, 532-nm optical pulses, of (A) a toluene solution of C_{60} and (B, C) THF solutions of a C_{60}-containing poly(1-phenyl-1-butyne) (sample from Table 2, no. 4); concentration (mg/mL)/linear transmission (%): (A) 0.16/43, (B) 1.50/56, (C) 3.00/43.

transmitted from the THF solution of the C_{60}−PPP starts to deviate from the linear transmission line. The transmitted fluence further departs from the linear line with the increase in the incident fluence and appears to level off at 149 mJ/cm^2 (saturation fluence). The toluene solution of C_{60} displays a saturation fluence of 257 mJ/cm^2. Thus, compared to the parent C_{60}, the C_{60}−PPP is a much better optical power limiter, possessing a higher linear transmittance but a lower saturation fluence, a step closer to a practically viable optical limiter. At the same level of linear transmittance (43%), the C_{60}−PPP solution gives a much lower saturation fluence (96 mJ/cm^2) than does the C_{60} solution (257 mJ/cm^2), once again proving that the C_{60}−PPP is an excellent optical power limiter. The other C_{60}−PPPs with different C_{60} contents all show superior optical limiting performance.

Similarly, the C_{60}−PPBs also effectively limit the strong laser pulses. Again, compared to the solution of the parent C_{60}, the C_{60}−PPB solutions show higher or same linear transmittance but lower saturation fluence. It is of interest to note that a C_{60}−PPB solution with an effective C_{60} concentration of 0.12 mg/mL exhibits a lower saturation fluence (Figure 11B) than does the C_{60} solution with a higher concentration (0.16 mg/mL; Figure 11A). Different from the PPP cousin, PPB absorbs the visible light of 532 nm. The electronic interaction in the ground and/or excited states between the C_{60} cages and the PPB chains may have contributed to the enhanced optical limiting power of the C_{60}−PPB. Schick et al. have found that, despite the unusual fluorescence emission from the hexapyrrolidine derivatives of C_{60}, the multiadducts still enjoy very efficient intersystem crossing from the first excited singlet manifold to the long-lived triplet state.[41] Due to the similarity in the multiple addition and in the fluorescence behavior, the C_{60}−PPB system may also still have a populated triplet state and thus the optical limiting may still be caused by the reverse saturable absorption mechanism, although much needs to be done to understand the interesting photophysical phenomena observed in these systems.

Concluding Remarks

Many groups have prepared numerous metallofullerene complexes, almost none of which have, however, found any practical applications.[1d,e] In this study, we have discovered a practically useful catalytic property of C_{60}: its addition to WCl_6−Ph_4Sn converts the metallic mixture from a poor initiator to an effective catalyst for the phenylalkyne polymerization. We have also succeeded in linking the C_{60} cages with the polyacetylene chains. Our process involves only a one-pot experimental procedure: Simply stirring a mixture of C_{60} and phenylalkyne in the presence of the W catalyst gives the C_{60}-containing polyacetylenes with high molecular weights in high yields.

The C_{60}-containing polyacetylenes exhibit unique optical properties. The C_{60}−PPBs emit strong blue light upon photoexcitation, representing the first examples of highly luminescent fullerene polymers. Both the C_{60}−PPPs and −PPBs effectively attenuating the power of the pulsed laser beam, with their saturation fluence being much lower than that of C_{60} at the similar linear transmittance. The fullerene polyacetylenes are stable, readily dissolve in common solvents, and can be easily cast into mechanically strong films. Such attributes, coupled with their unique optical properties, make the polymers promising candidates for advanced materials for hi-tech applications.

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