

# Synthesis and light-emitting properties of C<sub>60</sub>-containing poly(1-phenyl-1-butyne)s

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## Abstract

While WCl<sub>6</sub>–Ph<sub>4</sub>Sn is a poor catalyst for the polymerization of 1-phenyl-1-butyne (PB) at room temperature, it effectively polymerizes PB in the presence of C<sub>60</sub>, giving high molecular weight polymers in high yields. The polymers are soluble in common solvents such as THF and chloroform, and spectroscopic analysis reveals that C<sub>60</sub> has copolymerized with PB. Thus, C<sub>60</sub> plays the dual roles of comonomer and cocatalyst in the acetylene polymerization. While it has often been reported that C<sub>60</sub> quenches photoluminescence (PL) of conjugated copolymers, the C<sub>60</sub>-containing polyacetylene emits strong blue light, whose intensity is about two times higher than that of the PL of the parent PPB. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** C<sub>60</sub>-containing polyacetylene; Poly[C<sub>60</sub>-co-(1-phenyl-1-butyne)]; C<sub>60</sub>; Photoluminescence

## 1. Introduction

Since the discovery of the methods for mass production of fullerenes [1], there has been great interest in the development of fullerene-containing polymeric materials [2–14] because suitably designed fullerene polymers not only possess good processability but also exhibit interesting material properties. We have developed simple polymer reactions with general applicability for directly attaching C<sub>60</sub> to preformed polymers [15,16]. Polyacetylene is a prototypical conjugated polymer, and substituted polyacetylenes have been found to possess interesting material properties such as optical activity and liquid crystallinity [17–20]. Incorporation of C<sub>60</sub> into polyacetylenes is of interest because the  $\pi$ – $\pi$  interaction between the C<sub>60</sub> cages and the polyacetylene chains may impart intriguing electronic and optical properties to the C<sub>60</sub>-acetylene polymers. In this study, we tried to copolymerize C<sub>60</sub> and 1-phenyl-1-butyne (PB). Many groups have reported that C<sub>60</sub> quenches photoluminescence (PL) of conjugated polymers; we have, however, found that C<sub>60</sub> boosts the PL efficiency of the polyacetylene.

## 2. Experimental

High-purity (99.95%) C<sub>60</sub> was purchased from MER and kept in the dark before use. PB was purchased from Farchan, distilled from calcium hydride in vacuo, and stored in sealed ampoules in a dark and cold place. Tungsten(VI) chloride and tetraphenyltin (both Aldrich) were used as received without further purification. Toluene was purchased from Aldrich, dried over 4 Å molecular sieves, and distilled from sodium benzophenone ketyl immediately prior to use. Technical grade methanol was used to precipitate the polymer products.

All polymerization reactions were carried out under nitrogen. In a typical run, 26 mg of C<sub>60</sub>, 40 mg of WCl<sub>6</sub> (0.10 mmol), and 51 mg of Ph<sub>4</sub>Sn (0.12 mmol) were added into a baked 20-ml Schlenk tube under nitrogen. Freshly distilled toluene (5 ml) and 0.5 ml (3.5 mmol) of purified PB were injected into the Schlenk tube by a syringe, under nitrogen, at room temperature under stirring. After stirring at room temperature 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. The filtrate was added dropwise into 400 ml of methanol under stirring to precipitate the polymeric product. The product was redissolved in THF and the resulting solution was centrifuged at 2000 rev./min for 16 min. The supernatant was added dropwise through a filter into hexane (ca. 400 ml). The precipitant

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Table 1  
Polymerization of 1-phenyl-1-butyne (PB) in the presence of C<sub>60</sub><sup>a</sup>

No.	C <sub>60</sub> /PB feed ratio (wt.%) <sup>b</sup>	Polymer yield (wt.%)	10 <sup>-3</sup> M <sub>w</sub> (g/mol) <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	C <sub>60</sub> content <sup>d</sup>
1	0	2.1	262	2.4	0
2	0.9	83.1	168	2.2	2.8
3	4.4	85.1	374	2.2	3.9
4	5.7	87.9	529	3.1	7.9

<sup>a</sup> Catalyzed by WCl<sub>6</sub> (40 mg) and Ph<sub>4</sub>Sn (51 mg) in toluene (5 ml) under nitrogen at room temperature for 24 h.

<sup>b</sup> Feed amount of PB: 0.5 ml.

<sup>c</sup> Estimated by GPC on the basis of a polystyrene calibration.

<sup>d</sup> Estimated by IR analysis.

was collected and then dried under vacuum at 40°C to a constant weight. A gray-colored powder was obtained in 87.9 wt.% yield, whose C<sub>60</sub> content was estimated to be 7.9 wt.%.

FTIR spectra were measured on a Perkin–Elmer 16 PC spectrophotometer (KBr). UV–vis absorption spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer using a 1-cm<sup>2</sup> quartz cell. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX300 spectrometer using chloroform-*d* as the solvent. Molecular weights of the polymers were estimated by a Waters gel permeation chromatograph (GPC). Photoluminescence spectra were recorded on a SLM Aminco JD-490 spectrofluorometer.

### 3. Results and discussion

WCl<sub>6</sub>–Ph<sub>4</sub>Sn is an ineffective catalyst for the polymerization of PB in toluene at room temperature, yielding little amount (2.1%) of polymer (Table 1, no. 1). When the polymerization was conducted in the presence of a small amount of C<sub>60</sub>, a polymer with a high molecular weight was

produced in a high yield (83.1%; Table 1, no. 2), suggesting that C<sub>60</sub> acts as a cocatalyst, which enhances the catalytic activity of WCl<sub>6</sub>–Ph<sub>4</sub>Sn. We further found that C<sub>60</sub> was completely consumed in the polymerization reaction, thus, C<sub>60</sub> also acts as a comonomer at the same time, giving a copolymer of C<sub>60</sub> and PB. Increasing the feed ratio of C<sub>60</sub> increases the yield, M<sub>w</sub> and C<sub>60</sub> content of the resulting copolymer. When the C<sub>60</sub> feed ratio is 5.7%, a poly(C<sub>60</sub>-*co*-PB) with an M<sub>w</sub> of 529 000 and a C<sub>60</sub> content of 7.9% is obtained in a 87.9% yield.

Fig. 1 shows the FTIR spectra of C<sub>60</sub>, PPB and poly(C<sub>60</sub>-*co*-PB). Although the spectra of the homopolymer PPB and copolymer poly(C<sub>60</sub>-*co*-PB) look similar, closer inspection reveals some difference. The homopolymer does not absorb below 600 cm<sup>-1</sup>. The copolymer, however, shows an absorption band at 526 cm<sup>-1</sup>, which is, by comparison with the spectrum of C<sub>60</sub>, clearly due to the absorption of the C<sub>60</sub> moiety in the copolymer.

The electronic absorption spectra of C<sub>60</sub>, PPB and

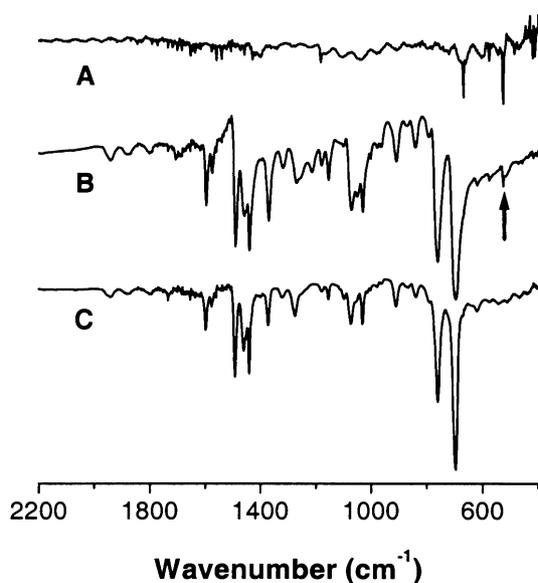


Fig. 1. IR spectra of (A) C<sub>60</sub>, (B) poly[C<sub>60</sub>-*co*-(1-phenyl-1-butyne)] (Table 1, no. 4), and (C) poly(1-phenyl-1-butyne) (Table 1, no. 1).

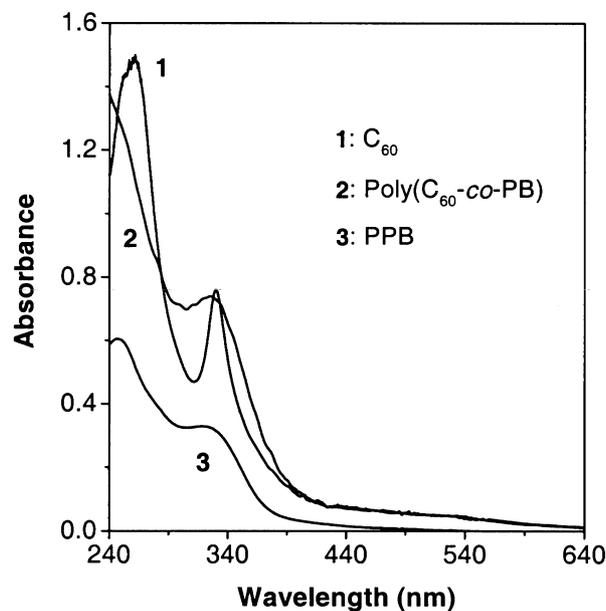


Fig. 2. UV spectra of THF solutions of poly(1-phenyl-1-butyne) (Table 1, no. 1), C<sub>60</sub>, and poly[C<sub>60</sub>-*co*-(1-phenyl-1-butyne)] (Table 1, no. 4); concentration (mg/ml): 0.013 (PPB), 0.020 (C<sub>60</sub>), 0.013 [poly(C<sub>60</sub>-*co*-PB)].

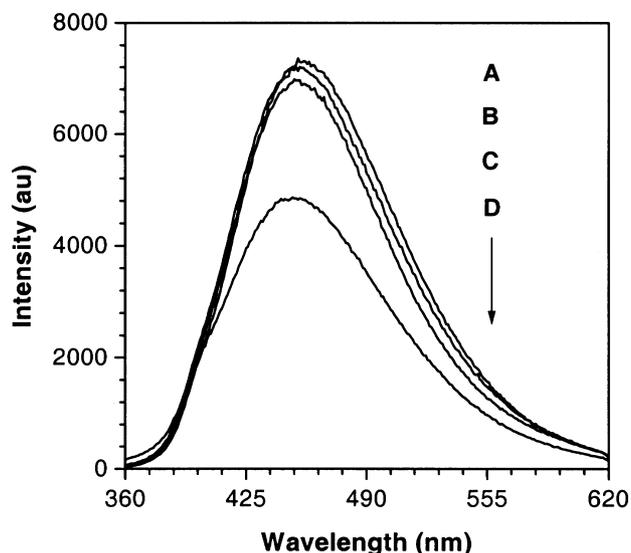


Fig. 3. Photoluminescence spectra of THF solutions of poly[C<sub>60</sub>-co-(1-phenyl-1-butyne)]s excited at 320 nm; C<sub>60</sub> content (wt.%): (A) 2.6, (B) 3.9, (C) 7.9; concentration (mg/ml): (A) 0.012, (B) 0.017, (C) 0.017. The spectrum of a THF solution of poly(1-phenyl-1-butyne) with a concentration of 0.016 (D) is shown for comparison.

poly(C<sub>60</sub>-co-PB) are shown in Fig. 2. PPB weakly absorbs at 246 and 319 nm and C<sub>60</sub> strongly absorbs at 255 and 330 nm. The UV spectrum of the poly(C<sub>60</sub>-co-PB) shows an absorption shoulder at ca. 250 nm and a strong absorption peaks at 325 nm. This strong peak as well as the overall increase in the absorptivity clearly demonstrates that C<sub>60</sub> has been incorporated into the PPB chains.

The <sup>1</sup>H NMR spectrum of the poly(C<sub>60</sub>-co-PB) is identical to that of PPB, probably because the cyclic olefin moiety of C<sub>60</sub> have undergone the W-catalyzed ring-opening metathesis reaction, which does not generate fullereryl protons. The copolymer, however, shows an extremely broad peak in so-called fullerene region of δ 135–160 [21], further confirming that the C<sub>60</sub> molecules have copolymerized with the PB monomer.

PPB emits strong blue light with its spectrum centered at ~ 450 nm (Fig. 3). Light emission from all the C<sub>60</sub>-PB copolymers is more intense than from the parent PPB, in contrast to previous reports that C<sub>60</sub> effectively quenches PL of conjugated polymers. We have repeatedly measured the PL spectra of the copolymers and confirmed that the results were well reproducible within experimental error. Garcia-Garibay, Rubin and co-workers have recently synthesized highly luminescent low molecular weight C<sub>60</sub> derivatives [22]. Our work, thus, represents a new example of highly luminescent high molecular weight C<sub>60</sub> polymer. The high PL efficiency may be associated with the structural modification of C<sub>60</sub> cages by the polymerization reaction, although

much needs to be done in understanding the real cause and mechanism.

#### 4. Conclusions

In this study, we have succeeded in copolymerizing C<sub>60</sub> and PB under mild conditions and discovered novel PL property of the copolymers. While WCl<sub>6</sub>-Ph<sub>4</sub>Sn is a poor catalyst for the polymerizations of disubstituted acetylenes at room temperature, C<sub>60</sub> significantly boosts the activity of the W-catalyst. Our finding of the dual function of comonomer and cocatalyst of C<sub>60</sub> in the acetylene polymerization provides a new and versatile synthetic tool for the synthesis of fullerene-functionalized polyacetylenes. The high PL efficiency makes the copolymer a promising candidate for the advanced materials to be used in the electroluminescent devices and light-harvesting systems.

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