

Synthesis and light-emitting properties of C₆₀-containing poly(1-phenyl-1-butyne)s

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Abstract

While WCl₆–Ph₄Sn is a poor catalyst for the polymerization of 1-phenyl-1-butyne (PB) at room temperature, it effectively polymerizes PB in the presence of C₆₀, 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 C₆₀ has copolymerized with PB. Thus, C₆₀ plays the dual roles of comonomer and cocatalyst in the acetylene polymerization. While it has often been reported that C₆₀ quenches photoluminescence (PL) of conjugated copolymers, the C₆₀-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.

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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 C₆₀ 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 C₆₀ into polyacetylenes is of interest because the π – π interaction between the C₆₀ cages and the polyacetylene chains may impart intriguing electronic and optical properties to the C₆₀-acetylene polymers. In this study, we tried to copolymerize C₆₀ and 1-phenyl-1-butyne (PB). Many groups have reported that C₆₀ quenches photoluminescence (PL) of conjugated polymers; we have, however, found that C₆₀ boosts the PL efficiency of the polyacetylene.

2. Experimental

High-purity (99.95%) C₆₀ 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 C₆₀, 40 mg of WCl₆ (0.10 mmol), and 51 mg of Ph₄Sn (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 C₆₀^a

No.	C ₆₀ /PB feed ratio (wt.%) ^b	Polymer yield (wt.%)	10 ⁻³ M _w (g/mol) ^c	M _w /M _n ^c	C ₆₀ content ^d
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

^a Catalyzed by WCl₆ (40 mg) and Ph₄Sn (51 mg) in toluene (5 ml) under nitrogen at room temperature for 24 h.

^b Feed amount of PB: 0.5 ml.

^c Estimated by GPC on the basis of a polystyrene calibration.

^d 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 C₆₀ 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-cm² quartz cell. ¹H and ¹³C 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

WCl₆–Ph₄Sn 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 C₆₀, a polymer with a high molecular weight was

produced in a high yield (83.1%; Table 1, no. 2), suggesting that C₆₀ acts as a cocatalyst, which enhances the catalytic activity of WCl₆–Ph₄Sn. We further found that C₆₀ was completely consumed in the polymerization reaction, thus, C₆₀ also acts as a comonomer at the same time, giving a copolymer of C₆₀ and PB. Increasing the feed ratio of C₆₀ increases the yield, M_w and C₆₀ content of the resulting copolymer. When the C₆₀ feed ratio is 5.7%, a poly(C₆₀-*co*-PB) with an M_w of 529 000 and a C₆₀ content of 7.9% is obtained in a 87.9% yield.

Fig. 1 shows the FTIR spectra of C₆₀, PPB and poly(C₆₀-*co*-PB). Although the spectra of the homopolymer PPB and copolymer poly(C₆₀-*co*-PB) look similar, closer inspection reveals some difference. The homopolymer does not absorb below 600 cm⁻¹. The copolymer, however, shows an absorption band at 526 cm⁻¹, which is, by comparison with the spectrum of C₆₀, clearly due to the absorption of the C₆₀ moiety in the copolymer.

The electronic absorption spectra of C₆₀, PPB and

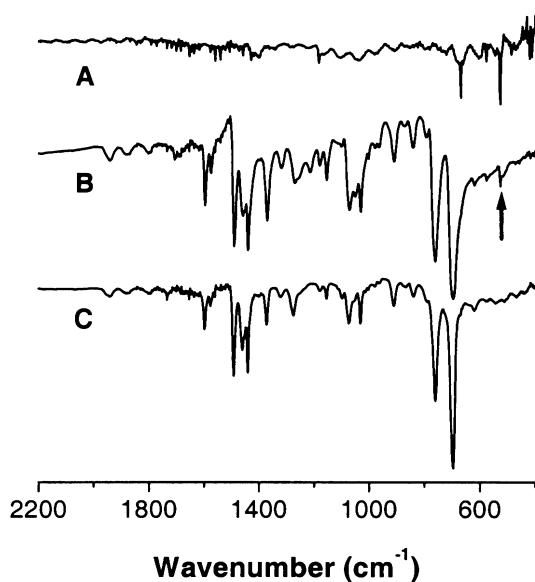


Fig. 1. IR spectra of (A) C₆₀, (B) poly[C₆₀-*co*-(1-phenyl-1-butyne)] (Table 1, no. 4), and (C) poly(1-phenyl-1-butyne) (Table 1, no. 1).

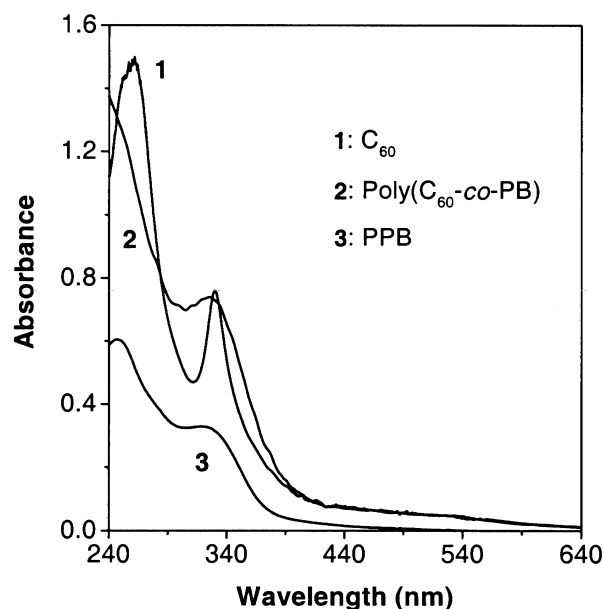


Fig. 2. UV spectra of THF solutions of poly(1-phenyl-1-butyne) (Table 1, no. 1), C₆₀, and poly[C₆₀-*co*-(1-phenyl-1-butyne)] (Table 1, no. 4); concentration (mg/ml): 0.013 (PPB), 0.020 (C₆₀), 0.013 [poly(C₆₀-*co*-PB)].

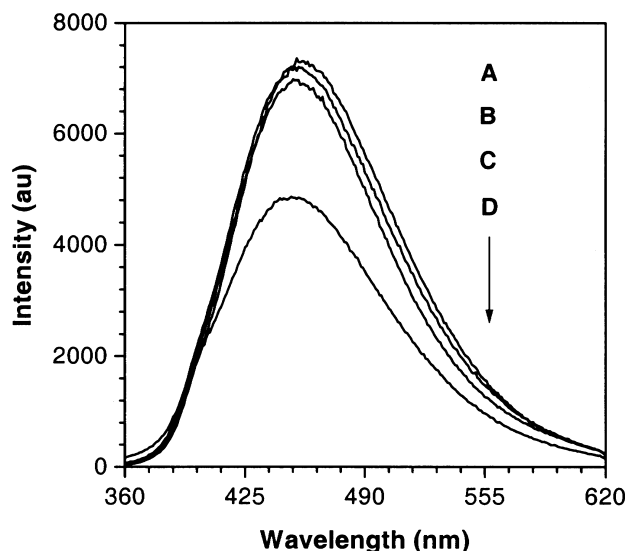


Fig. 3. Photoluminescence spectra of THF solutions of poly[C₆₀-co-(1-phenyl-1-butyne)]s excited at 320 nm; C₆₀ content (wt.%): (A) 2.6, (B) 3.9, (C) 7.9; concentration (mg/ml): (A) 0.012, (B) 0.017, (C) 0.017. The spectrum of a THF solution of poly(1-phenyl-1-butyne) with a concentration of 0.016 (D) is shown for comparison.

poly(C₆₀-co-PB) are shown in Fig. 2. PPB weakly absorbs at 246 and 319 nm and C₆₀ strongly absorbs at 255 and 330 nm. The UV spectrum of the poly(C₆₀-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 C₆₀ has been incorporated into the PPB chains.

The ¹H NMR spectrum of the poly(C₆₀-co-PB) is identical to that of PPB, probably because the cyclic olefin moiety of C₆₀ 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 C₆₀ 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 C₆₀-PB copolymers is more intense than from the parent PPB, in contrast to previous reports that C₆₀ 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 C₆₀ derivatives [22]. Our work, thus, represents a new example of highly luminescent high molecular weight C₆₀ polymer. The high PL efficiency may be associated with the structural modification of C₆₀ 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 C₆₀ and PB under mild conditions and discovered novel PL property of the copolymers. While WCl₆-Ph₄Sn is a poor catalyst for the polymerizations of disubstituted acetylenes at room temperature, C₆₀ significantly boosts the activity of the W-catalyst. Our finding of the dual function of comonomer and cocatalyst of C₆₀ 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.

Acknowledgements

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