

Synthesis and optical limiting in copolymers of C₆₀ and 1-phenyl-1-butyne

Hong Yao XU¹*, Shan Yi GUANG¹, Ben Zhong TANG²

¹Department of Chemistry, Anhui University, Hefei 230039

²Department of Chemistry, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong

Abstract: While WCl₆-Ph₄Sn is a poor catalyst for the polymerization of 1-phenyl-butyne (PB) at room temperature, it effectively polymerizes PB in the presence of C₆₀, giving high molecular weight polymers in high yields. The polymer is soluble in THF and chloroform and spectroscopic analysis reveals that C₆₀ has copolymerized with PB. Thus, C₆₀ plays dual roles of comonomer and cocatalyst in the acetylene polymerization. The copolymers strongly attenuate 532-nm laser pulses, whose limiting performance is superior to that of parent C₆₀.

Keywords: C₆₀, polyacetylene, fullerene polymer.

Since the discovery of the methods for mass production of fullerenes¹, there has been great interest in the development of fullerene-containing polymeric materials²⁻³ because suitably designed fullerene polymers not only possess good processability but also exhibit interesting materials properties⁴⁻⁵. We have also attached C₆₀ to polyphenylacetylene chains by a WCl₆-catalyzed copolymerization reaction⁶⁻⁷. In this letter, we chose an acetylene monomer, that is, 1-phenyl-butyne (PB), which can not be effectively polymerized by the W catalysts. We here demonstrate that C₆₀ acts as both comonomer and cocatalyst in the acetylene polymerization and measure its optical limiting performance of the poly[C₆₀-co-(1-phenyl-1-butyne)].

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 with 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 rpm for 16 min. The supernatant was added dropwise through a filter into hexane (*ca.* 400 mL). The precipitate was collected and dried under vacuum at 40 °C to constant weight. A gray-colored powder was obtained in 87.9 wt % yield, whose C₆₀ content was estimated to be 7.9 wt % based on IR analysis.

The homopoly(1-phenyl-butyne) (PPB) does not absorb below 600 cm⁻¹, while the FTIR spectrum of poly[C₆₀-co-(1-phenyl-1-butyne)] shows an absorption band at 526cm⁻¹, which is, by comparison with spectrum of C₆₀, clearly due to the absorption of

the C₆₀ moiety in the copolymer.

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 peak at 325 nm. This strong peak as well as the overall increase in the absorptivity clearly demonstrate that C₆₀ has been incorporated into the PPB chains.

While the ¹H NMR spectrum of the poly (C₆₀-co-PB) is similar to that of PPB, probably because the cyclic olefin moiety of C₆₀ undergoes ring-opening metathesis reaction, which does not generate fullereryl protons. The copolymer, however, shows an extremely broad peak in so-called fullerene region of (135-160 ppm), further confirming that the C₆₀ molecules have copolymerized with PB monomers.

The optical limiting responses of the poly (C₆₀-co-PB) with a C₆₀ content of 7.9 wt % were measured in THF solutions. In the low fluence region, the solution with a concentration of 1.50 mg/mL exhibits a high linear transmittance (56%) and the transmitted fluence linearly increases with the incident fluence. The transmitted fluence starts to deviate from linearity at the incident fluence of 147 mJ/cm² and saturates at 150 mJ/cm² with increase of the incident fluence. This clearly demonstrates that the absorption coefficient of the solution increases with incident fluence, which must be due to the reverse saturable absorption of the C₆₀ moiety in poly (C₆₀-co-PB) because PPB does not show the optical limiting property at the same and higher concentrations. The optical limiting behavior of the copolymer thus further confirms that C₆₀ cages are attached to the PPB chains.

In summary, we have succeeded in copolymerizing C₆₀ and PB under mild conditions and discovered excellent optical limiting 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 excellent optical limiting performance makes the copolymers promising candidates for the advanced materials to be used in the laser-based high-technology industries.

Acknowledgment

This work was in part supported by the National Natural Science Foundation of China and the Hong Kong Research Grants Council (HKUST 6062/98P and DAG 96/97.SCII)

References

1. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature*, **1990**, 347, 354.
2. I. Amato, *Science*, **1991**, 254, 30.
3. J. E. Fischer, *Science*, **1994**, 264, 1548.
4. B. Z. Tang, S. M. Leung, H. Peng, N. T. Yu, K. C. Su, *Macromolecules*, **1997**, 30, 2848.
5. B. Z. Tang, H. Peng, S. M. Leung, C. F. Au, W. H. Poon, H. Chen, X. Wu, M. W. Fox, N. T. Yu, H. Hiraoka, C. Song, J. Fu, W. Ge, K. L. G. Wong, T. Monda, F. Nemoto, K. C. Su, *Macromolecules*, **1998**, 31, 103.

6. H. Xu, B. Z. Tang, *Polym. Mater. Sci. Eng.*, **1999**, 80, 215.
7. H. Xu, B. Z. Tang, *J. Macromolecular Science, Pure Appl. Chem.*, **1999**, 36, 1197.

Received 21 June 1999