

Rapid Communications

**SYNTHESIS, CHARACTERIZATION AND OPTICAL PROPERTIES OF
THE COPOLYMERS OF C₆₀ AND 1-PHENYL-1-PROPYNE***

Hong-yao Xu and Ben-zhong Tang**

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

Abstract While WCl₆-Ph₄Sn fails to polymerize 1-phenyl-1-propyne (PP) at room temperature, high molecular weight (M_w up to 410×10^3) polymers are obtained in high yields (up to 80%) when the polymerizations of PP are carried out in the presence of C₆₀ using the W catalyst under the same conditions. The polymers are soluble in common organic solvents such as THF, chloroform, and toluene. Molecular structures of the polymers are characterized by FT-IR, UV, NMR, GPC and XRD, and it is found that C₆₀ is copolymerized with PP. Thus C₆₀ plays the dual roles of comonomer and cocatalyst in the polymerization reaction. C₆₀ contents of the copolymers can be easily changed by varying the C₆₀ amounts in the feed mixtures. The copolymers effectively limit strong 532 nm laser pulses, whose limiting performance is superior to that of parent C₆₀.

Keywords Substituted polyacetylenes, C₆₀, Poly[C₆₀-co-(1-phenyl-1-propyne)], Fullerene-functionalized polymers

INTRODUCTION

The polymerizations of (substituted) acetylenes were investigated by using various initiation systems^[1-6], including heat, light, radiation, and radical, ionic, and transition-metal catalysts. Ziegler-Natta catalysts, such as Ti(On-Bu)₄-Et₃Al and Fe(acac)₃-Et₃Al, can catalyze the polymerization of acetylene and some monosubstituted acetylenes^[1, 2]. Halides of niobium (Nb) and tantalum (Ta) are known to selectively cyclotrimerize acetylene and monosubstituted acetylenes (e.g., phenylacetylene and 1-hexyne)^[7, 8], while organoniobium and -tantalum complexes of M₂Cl₆(SC₄H₈)₃ (M = Nb, Ta) polymerize disubstituted acetylenes (1-phenyl-1-propyne, 3-hexyne, and 4-methyl-2-hexyne)^[9]. These complexes, however, are sensitive to air and rather difficult to prepare. MoCl₅ and organorhodium complexes can polymerize monosubstituted acetylenes but are unreactive to 1-phenyl-1-alkyne polymerizations. WCl₆-Ph₄Sn can polymerize monosubstituted acetylenes, but is ineffective for the polymerizations of disubstituted acetylenes. For example, polymerization of PP catalyzed by WCl₆-Ph₄Sn at 60°C gave a low-molecular-weight (3.9×10^3) polymer in a moderate yield while that conducted at room temperature did not yield any polymeric product^[10]. In our previous work, we found that C₆₀ copolymerized with monosubstituted acetylenes such as phenylacetylene^[11]. In this work, we tried to polymerize PP in the presence of C₆₀ using WCl₆-Ph₄Sn as catalyst at room temperature. We found that C₆₀ molecules were

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** Corresponding author: Ben-zhong Tang (唐本忠), E-mail: tangbenz@ust.hk

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consumed and played the dual roles of cocatalyst and comonomer. We report here the copolymerization of C_{60} and PP and the optical properties of the resulting poly[C_{60} -*co*-(1-phenyl-1-propyne)]s [poly(C_{60} -*co*-PP)s].

EXPERIMENTAL

Materials and Instrument

High-purity (99.95%) C_{60} was purchased from MER and kept in the dark. PP 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 from Aldrich) were used as received without further purification. Toluene was purchased from Aldrich and dried over 0.4 nm molecular sieves, and distilled from sodium benzophenone ketyl immediately before use. Technical grade methanol was used to precipitate the polymer products. All the polymerization reactions were carried out under nitrogen.

The ^1H and ^{13}C -NMR spectra were recorded on a Bruker ARX300 spectrometer using chloroform-*d* as solvent. FT-IR spectra were measured on a Perkin-Elmer 16 PC spectrometer (KBr). The UV-Vis absorption spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer using a 1 cm square quartz cell. The molecular weights of the polymers were estimated by a Waters gel permeation chromatograph (GPC) with a differential refractometer (RI) and an ultraviolet (UV) detector, using tetrahydrofuran (THF) as eluent. The X-ray diffraction (XRD) patterns were obtained from a Philips PW 1830 powder diffractometer with a graphite monochromator using 0.15406 nm CuK_α wavelength at room temperature (scanning rate 0.02°/s, scan range 3~27°).

Polymerization

In a typical run, 30 mg of C_{60} , 84 mg of tungsten(VI) chloride (0.21 mmol) and 102 mg of tetraphenyltin (0.24 mmol) were added into a heated 20 mL Schlenk tube under nitrogen. Freshly distilled toluene (5 mL) and 0.56 mL (4.8 mmol) of purified PP were injected into the Schlenk tube by a syringe under nitrogen at room temperature with stirring. After constant 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 with a cotton filter. The soluble 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. 300 mL). The precipitant was collected and then dried under vacuum at 40°C to a constant weight. A gray-colored powder was obtained in 56.8% yield, whose C_{60} content was estimated to be 9.1 wt%.

Optical Limiting Measurement

The optical limiting experiments were performed at 532 nm with 8-ns pulses generating 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 onto a 1 cm square quartz cell filled with a THF solution of polymer (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

It is known that $\text{WCl}_6\text{-Ph}_4\text{Sn}$ is ineffective at room temperature to the polymerization of PP in

toluene^[10], which is further confirmed by our experiment (Table 1, No. 1). We tried to polymerize PP in the presence of C₆₀ at room temperature. Surprisingly, after 24 h of stirring, the polymerization gave a high molecular weight polymer in a high yield. Thus, C₆₀ acts as a cocatalyst, enhancing the catalytic activity of WCl₆-Ph₄Sn. We further found that C₆₀ was consumed in the polymerization reaction. Thus C₆₀ also acts as a comonomer at the same time, giving a copolymer of C₆₀ and PP [poly(C₆₀-co-PP)]. By varying the C₆₀ feed ratio, the copolymers with C₆₀ contents of 3.8–9.1 wt % were obtained. GPC analysis shows that the parent poly(1-phenyl-1-propyne) (PPP) isolated from the WCl₆-Ph₄Sn system at room temperature has a broad molecular weight distribution. The PPP is completely soluble in THF, but the yield of the polymerization is very low (0.5%). In contrast, the yields of the copolymers obtained from the WCl₆-Ph₄Sn/C₆₀ system at room temperature are much higher (up to 80.3 wt %).

Table 1 Polymerization of 1-Phenyl-Propyne (PP) in the Presence of C₆₀^a

No.	PP (mL)	C ₆₀ (mg)	C ₆₀ /PP (mol %)	WCl ₆ (mg)	Ph ₄ Sn (mg)	Yield (%)	<i>M_w</i> /10 ³ ^b	<i>M_w</i> / <i>M_n</i>	C ₆₀ content ^c (wt %)
1	0.50	0	0	20	17	0.5	886	109.0	0
2	0.55	12	0.38	82	100	75.0	137	15.7	3.8
3	0.56	21	0.65	86	99	80.3	409	35.4	6.2
4	0.60	30	0.87	84	102	56.8	44	4.5	9.1

a) under nitrogen in toluene (5 mL) at room temperature for 24 h; b) estimated by GPC on the basis of a polystyrene calibration; c) estimated by IR analysis.

Figure 1 shows the FT-IR spectra of C₆₀, PPP and poly(C₆₀-co-PP). Although the spectra of the homopolymer and copolymer look similar, careful analysis shows some distinctions. The characteristic peaks of C₆₀ at 526, 574, and 668 cm⁻¹ appear to remain unaffected after being incorporated into the copolymer. The peak of C₆₀ at 1184 cm⁻¹ can also be seen in the spectrum of the copolymer.

The electronic spectra of C₆₀, PPP and poly(C₆₀-co-PP) are shown in Fig. 2. The PPP absorption is a continuously descending featureless curve except a small shoulder peak at wavelength of ca. 330 nm. The main absorption peaks of C₆₀ are located at 255 and 330 nm. The UV spectrum of the poly(C₆₀-co-PP) shows shoulder peaks at 256 and 330 nm, corresponding to the absorption peaks of C₆₀, further confirming that C₆₀ has been incorporated into the PPP chains.

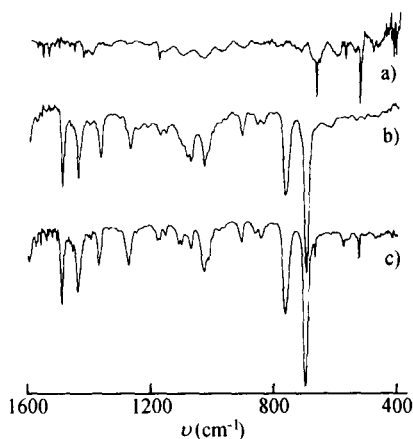


Fig. 1 IR spectra of a) C₆₀, b) poly(1-phenyl-1-propyne) (sample from Table 1, No. 1), and c) poly[C₆₀-co-(1-phenyl-1-propyne)] (Table 1, No. 4)

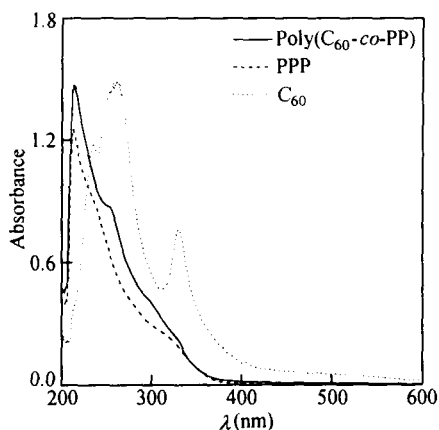


Fig. 2 UV spectra of THF solutions of poly[C₆₀-co-(1-phenyl-1-propyne)] (sample from Table 1, No. 4), poly(1-phenyl-1-propyne) (Table 1, No. 1), and C₆₀; concentration (mg/mL): 0.013 [poly(C₆₀-co-PP)], 0.013 (PPP), and 0.020 (C₆₀)

The C₆₀-PP copolymers were characterized by ¹H and ¹³C-NMR spectroscopy. The proton signals of the copolymer are largely due to PPP structure with broad peaks in aliphatic ($\delta = 1\sim 2.5$) and aromatic ($\delta = 6.0\sim 7.5$) regions. The broad peaks of the copolymer in aliphatic and aromatic region are separated into three peaks, respectively. The ratios of integration of aromatic ring proton peaks are 1.0 ($\delta = 6.9$) : 0.63 ($\delta = 6.76$) : 0.26 ($\delta = 6.4$), which are different from the relative population of the aromatic protons. The broad peaks in aliphatic protons are also separated into three peaks. Their integration ratios are 0.47(δ 1.69) : 0.50 (δ 1.57) : 0.28 (δ 1.26). The relative population of the aliphatic and the aromatic protons is consistent with the ratio of integration of the aromatic protons to that of the aliphatic ones in the copolymer. We thus suspect that the copolymer has three kinds of different conformation.

In the ¹³C-NMR spectra of the copolymer, besides the carbon signals of PPP, an extremely broad peak in the so-called fullerene region ($\delta = 135\sim 160$)^[12] was found. The double bond carbon signal of main chains in the region of $\delta = 133\sim 135$ is almost unchanged.

The XRD pattern of the poly(C₆₀-co-PP) is shown in Fig. 3 along with those of the parent PPP and C₆₀. The pure C₆₀ displays four Bragg reflection peaks at 2θ of 10.92°, 17.72°, 20.90°, and 21.80°, corresponding respectively to the d -spacings of 0.81, 0.50, 0.43 and 0.41 nm^[13-15]. The XRD pattern of PPP shows two diffuse halos centered at 2θ of 10.7° and 19.98°. Two broad amorphous halos of PPP are seen in the XRD diagram of poly(C₆₀-co-PP). In addition, the C₆₀-PP copolymer displays three new minor peaks centered at 2θ of 20.84° ($d = 0.429$ nm), 17.64° ($d = 0.502$ nm), and 10.62° ($d = 0.832$ nm). The reflection positions of C₆₀ in the C₆₀-PP copolymer shift to lower angles (or larger d values) than the parent C₆₀. The enhancement in spacing can be attributed to the copolymerization of C₆₀ with PP, further proving that C₆₀ molecules have incorporated into the copolymer chains.

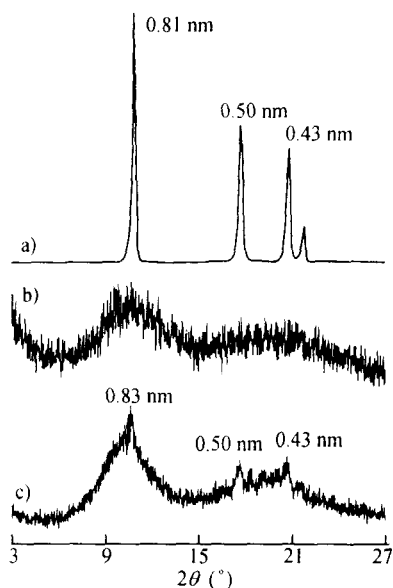


Fig. 3 XRD patterns of a) C₆₀, b) poly(1-phenyl-1-propyne) (sample from Table 1, No. 1), and c) poly[C₆₀-co-(1-phenyl-1-propyne)] (Table 1, No. 4)

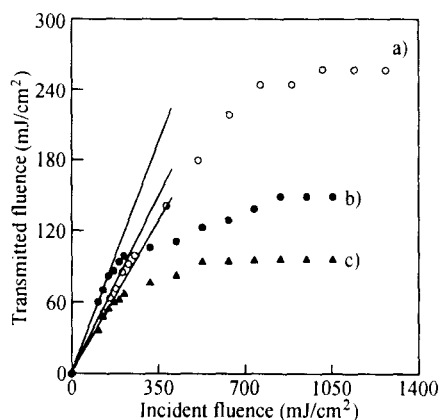


Fig. 4 Optical limiting responses to 8 ns, 532 nm laser pulses, of a) toluene solution of C₆₀ and b, c) THF solutions of poly[C₆₀-co-(1-phenyl-1-propyne)] (sample from Table 1, No. 4); concentration (mg/mL)/linear transmission (%): a) 0.16/43; b) 6.0/56; c) 9.5/37

Figure 4 shows the optical limiting behavior of the poly(*C*₆₀-*co*-PP) solutions in THF and of a *C*₆₀ solution in toluene. In the low fluence region, the poly(*C*₆₀-*co*-PP) solution with a concentration of 6.0 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. In the high incident fluence region, the transmitted fluence reaches a plateau and is saturated at 149 mJ/cm². The transmitted fluence remains unchanged in the low incident fluence region but rapidly decreases with the incident fluence when the solution is subjected to high-intensity radiation. This clearly shows that the absorption coefficient of the solution increases with increasing incident fluence. Thus the optical limiting in the poly(*C*₆₀-*co*-PP) solution originates from the reverse saturable absorption of the *C*₆₀ moiety in the copolymer because the parent PPP does not exhibit the optical limiting property at the same or even higher concentration. The optical limiting behavior further confirms that *C*₆₀ cages are attached to the PPP chains. Compared with the *C*₆₀ solution in toluene with a linear transmittance of 43%, the copolymer solution shows superior optical limiting properties although its linear transmittance is higher (56%). Similarly, the poly(*C*₆₀-*co*-PP) solution with a concentration of 9.5 mg/mL effectively limits the optical pulses, showing a saturation fluence as low as 96 mJ/cm².

CONCLUSION

In this study, we discovered the cocatalyst effect of *C*₆₀ in the polymerization of PP catalyzed by WCl₆-Ph₄Sn and succeeded in synthesizing the copolymers of *C*₆₀ and PP in a controllable manner at room temperature. Our finding of the dual roles of comonomer and cocatalyst of *C*₆₀ provides a novel catalyst system for the polymerizations of disubstituted acetylenes and enables the synthesis of a wide variety of new copolymers of *C*₆₀ and acetylenes. The excellent optical limiting performance makes the copolymers a promising candidate for advanced materials usable in the laser-based high-technology industries.

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