## **Preliminary Note**

## New soluble poly(fluoro-diacetylene)s with a large $\pi$ conjugation system

YaDong Zhang and JianXun Wen\*

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032 (China)

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## Abstract

New soluble poly(fluoro-diacetylene)s with fluoro-aromatic rings directly bound to an extended  $\pi$ -conjugated backbone have been generated via solid-state polymerization induced by thermal annealing. The large  $\pi$ -conjugated backbones of these soluble poly(fluoro-diacetylene)s have been established by means of UV–vis spectra.

In recent years, there has been much interest in polydiacetylenes that show large third-order non-linear optical susceptibilities  $\chi^{(3)}$  [1-4] derived from  $\pi$ -electron delocalization of the polydiacetylene main chains. It is well known that the  $\chi^{(3)}$  values of polydiacetylenes obey the relationships given in eqn. (1) as far as energy gap is concerned [5]. To date, quite a number of insoluble polydiacetylenes with methylene groups between the main chain and side-groups [6] and soluble polydiacetylenes having flexible chains (polymethelene groups) between the main chain and side-groups [7-10] have been reported. To obtain larger  $\chi^{(3)}$  values, polydiacetylenes with increased numbers of  $\pi$ -electrons might be better candidates. However, in general, most such diacetylene monomers appear not to polymerize in the solid state [11]. Recently, we have shown that poly(fluoro-diacetylene)s (A) with three flexible substituents on each polyfluorophenyl ring are soluble in common organic solvents, such as CHCl<sub>3</sub> and THF, giving red polydiacetylene solutions. When poor solvents, such as methanol, were added to these red polydiacetylene solutions, the colour of the solution changed from red to blue [12, 13]. Here, we wish to report some new results regarding soluble poly(fluorodiacetylene)s without flexible chains on their side-groups (see Scheme 1)

$$\chi^{(3)} \alpha E_g^{-6} \tag{1}$$

Fluoro-diacetylene monomers, 1,4-bis(2,4,6-triaryloxy-3,5-difluorophenyl)butadiynes (**4a**-**c**) were prepared via the procedure reported previously



$$R = p - CH_3(CH_2)_n CH_2 - C_6H_4O - , p - CH_3(CH_2)_n CH_2O - C_6H_4O -$$





(2a-c)



**c**,  $R = p - BrC_6 H_4 0$ .

Scheme 1.

[13, 14]. When the white fluoro-diacetylene crystals  $4\mathbf{a}-\mathbf{c}$  were polymerized in the solid state by thermal annealing at 160 °C for 147 h, the crystal colour changed from colourless to deep blue. We have found that these blue crystals are soluble in THF or DMF to yield blue solutions, but pure poly-(4a-c) cannot be obtained using a monomer (solvent)-polymer (non-solvent) system. Further work on this matter is in progress.

We consider that this blue colour is due to the extensive  $\pi$ -conjugated backbone of poly-(**4a–c**), which may be observed more quantitatively in the UV–vis spectra shown in Fig. 1. The UV–vis spectra of the polymerized crystals derived from **4a–c** by thermal annealing were measured as solutions in THF. Before annealing, samples **4a–c** exhibited no absorption bands over the range 450–800 nm, but after thermal treatment absorption bands appeared within this range [see curves depicted in Fig. 1]. These figures show that the absorption maximum of poly-**4a** was shifted to 640 nm, i.e., to a longer wavelength than soluble polydiacetylenes [9, 10] and insoluble polydiacetylenes, such as PTS [15] and poly-TCDU [16]. The absorption edges of poly(**4b–c**) were similarly shifted to 800 nm. In other words, the band gap (the energy difference between the HOMO and LUMO) of these polydiacetylenes is apparently smaller than that for known soluble and insoluble polydiacetylenes. Hence it may be considered that these polydiacetylenes in which fluoro-aromatic rings are directly bound to the  $\pi$ -conjugated main chain,



Fig. 1. UV-vis absorption spectra of (A) poly-4a, (B) poly-4b and (C) poly-4c in THF solution.

provide a more extensive  $\pi$ -conjugated system and larger third-order nonlinear optical susceptibilities than observed previously. The wavelength of the absorption edge and the maximum in the spectrum for poly-4a are smaller than those for poly-(4b-c) due to the shorter conjugated  $\pi$ -electron length of poly-4a.

Polydiacetylenes are generally insoluble even in exotic organic solvents and cannot be characterized via normal polymer characterization techniques. Hence it is difficult to prepare them in a suitable sample form (such as a film) for THG measurements. On possible method of increasing the solubility of polydiacetylene would be to attach flexible side-chains to the polydiacetylene backbone. This principle has been tested successfully with polydiacetylenes [7–10], and indeed we have shown that side fluoro-aromatic rings with flexible chains attached to the polydiacetylene backbone are capable of improving the solubility of polydiacetylenes [12, 13]. It is noteworthy that some polydiacetylenes with large side-groups attached to the backbone are even soluble in common organic solvents. The improved solubility of polydiacetylenes arising from the procedure described could lead to the preparation of suitable films for non-linear optical purposes.

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