

The syntheses of a soluble diacetylene and its polymer with push–pull azobenzene and pyrimidine ring attached

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Abstract

A new unsymmetrical polydiacetylene having a pyrimidine ring and an azobenzene chromophore directly bound to the two ends of a diacetylene moiety was synthesized with good yield. The diacetylene monomer could easily dissolve in common organic solvents, and be polymerized thermally or under light illumination. Micro and macroscopic third-order susceptibilities were estimated for the yielded polymer. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Polydiacetylenes are of particular interest for their large optical nonlinearities and fast excited-state relaxation times. Its general formula $(=CR-C\equiv C-CR=)_n$ is a model system of conjugated π -electrons in one dimension, extensive electron delocalization along the chain direction endows them a metal wire-like conductive property. At the meantime, for various possible linear and nonlinear optical applications, in order to modulate, or to modify the propagation manner of the electron signal on the backbone of the polymer, it is ideal to incorporate covalently a photosensitive chromophore in polydiacetylene to act as an ‘antenna’ to receive light signal. Azobenzene unit is such a most effective and important chromophore. Only few publications about polydiacetylenes containing azobenzene chromophore, especially about such soluble polymer, have appeared in the literature up to now [1]. In this paper, we

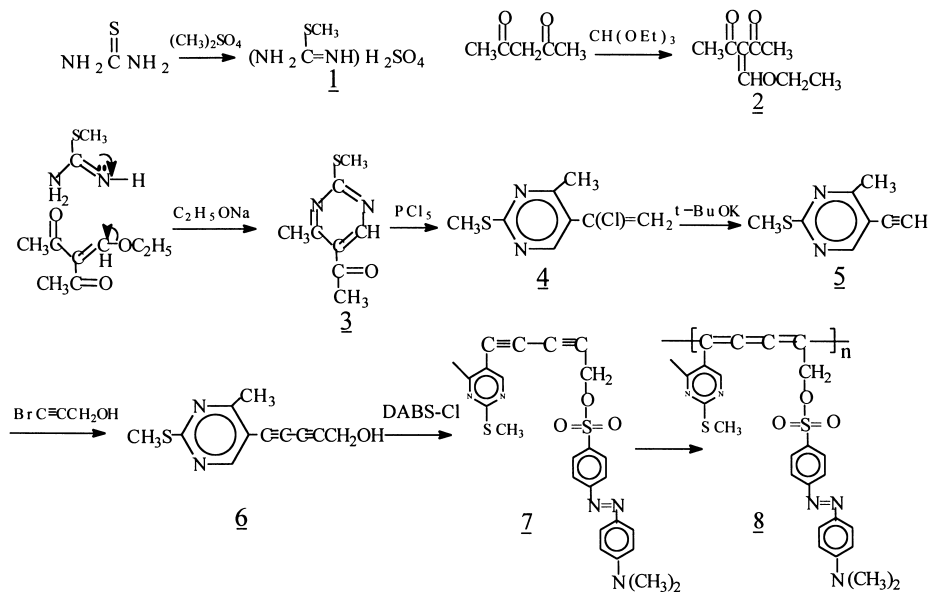
are going to report the syntheses of a novel soluble diacetylene with push–pull azobenzene substituted and corresponding polydiacetylene. A pyrimidine ring has been designed and introduced to the system to improve processibility of the diacetylene.

2. Experimental

Instruments employed were IR (BIO-RAD FTS-165), UV–Vis (1601PC SHIMADZU), MS (Trio-2000), ¹H NMR (Varian Gemini 300 operating at 300 MHz) spectrophotometers, and element analyzer (Heraeus CHN-RAPID). Solvents such as acetone and THF were distilled from sodium and LiAlH₄; methanol and benzene were distilled from magnesium methoxide; *n*-butylamine was further purified by distillation. They were stored in a drybox before use. The catalyst cuprous chloride was treated with dilute sulfuric acid for three times prior to use. Methyl-isothioureia sulfate (1) [2,3] and 2,4-Dimethyl-amino-azobenzene-4-sulfonyl chloride (DABS-Cl) [4] were prepared following the procedure described in the references. The general scheme of our synthesis is shown below.

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2.1. Acetylacetonyl ethoxy methane (2)

A mixture of acetylacetone (100 g, 1.0 mol), triethyl orthoformate (260 g, 1.75 mol), and acetic anhydride (291 g, 2.84 mol) was refluxed with stirring for 1 h at 120°C, 130°C and 140°C, respectively. The solvent and unreacted acetic anhydride and triethyl orthoformate were removed by rotatory evaporator, the residue was vacuum distilled and 136 g of **2** was collected as a light yellow liquid at 132–134°C/1.3 kPa, yield 87.5%. IR (KBr): 2950 (–CH₂–, –CH₃), 1660(–CO–) cm^{–1}.

2.2. 5-Acetyl-6-methyl-2-methylthio-pyrimidine (3)

To a round-bottom flask with absolute ethyl alcohol (1000 ml), sodium (25.3 g, 1.1 mol) was added, after reaction was completed, the solution was cooled to 0°C, then **1** (139 g, 0.5 mol) and **2** (156 g, 1.0 mol) were added successively. The solution was stirred at room temperature for 1 h and then refluxed for 1 h. The Na₂SO₄ formed during the reaction was removed from the reaction mixture by filtration while it was hot. The filtrate was put aside for another 24 h and then the crude product was separated by filtration, and recrystallized in 95% ethyl alcohol to give 127.5 g of **3** as a white solid. Yield: 70%, m.p.: 82–83°C. IR (KBr): 3000, 2900(–CH₃), 1680(–CO–), 1510, 1400 (pyrimidine ring) cm^{–1}.

2.3. 5-(1'-Chloroethylene)-6-methyl-2-methylthio-pyrimidine (4)

A solution of **3** (91 g, 0.50 mol), and phosphoric chloride (PCl₅) (125 g, 0.60 mol) in dry benzene (1500

ml) was refluxed for 3 h, and cooled to room temperature, then poured onto lots of cracked ice, neutralized with sodium carbonate saturated solution to pH = 7. Water phase that separated from benzene was extracted with benzene (3 × 150 ml), the resulting mother liquor was evaporated at evaporator first and then further distilled under reduced pressure. A clear liquid, the distillate at 120–122°C/6.6 kPa was identified to be the product **4**, weight 71 g, yield 71%. IR (KBr): 3000, 2950(–CH₃, =CH₂), 1620(–C=C–), 1550, 1500, 1400(pyrimidine ring) cm^{–1}. MS (EI, %) *m/z*: 201(M⁺ + 1). Element Analysis: Calculated for C₈H₉N₂SCl: C, 47.88; H, 4.52; N, 13.96; Found: C, 47.78; H, 4.53; N, 13.90.

2.4. 5-Ethynyl-6-methyl-2-methylthio-pyrimidine (5)

A solution of **4** (100.3 g, 0.5 mol) in anhydrous ether (800 ml) was cooled to 0°C. Another solution of t-BuOK/t-BuOH (1 M, 550 ml) was added dropwisely to the above solution. The mixture was stirred for 4 h at room temperature. After removing the solvent by evaporation, the residue was further distilled by steam-distillation to afford 59 g of **5** as a white solid. Yield: 72%. m.p.: 72–73°C. IR (KBr): 3150(C≡CH), 2100(C≡C), 1550, 1500, 1400 (pyrimidine ring) cm^{–1}. MS (EI, %) *m/z*: 165(M⁺ + 1,98). Element Analysis: Calculated for C₈H₉N₂SCl: C, 58.50; H, 4.92; N, 17.06; Found: C, 58.41; H, 4.91; N, 16.99.

2.5. 5-(p-methylthio-o-methyl-pyrimidinyl)-2,4-pentadiyn-1-ol (6) [5]

Under nitrogen, after a mixture of cuprous chloride (1.0 g, 5 mmol), *n*-C₄H₉NH₂ (60 ml) and THF/CH₃OH

Table 1
UV assistant polymerization of monomer **7** to polymer **8**

Sample	7 + Substrate/g	8 + Substrate/g	7 /g	8 /g	Time/min	Conversion ratio, %
1	3.4434	3.4366	0.0113	0.0045	10	39.8
2	3.2853	3.2798	0.0111	0.0056	30	50.6
3	3.5552	3.5501	0.0117	0.0066	50	56.4
4	3.3528	3.3487	0.0095	0.0054	300	57.0

($V/V = 1:1$, 400 ml) was cooled to 0°C , hydroxyamine hydrochloride (20 g, 0.288 mol), and **5** (41.0 g) were added in turn. When a white precipitate appeared, a solution of 3-bromopargyl alcohol [6] (0.35 mol) in THF/ CH_3OH ($V/V = 1:1$, 400 ml) was added dropwisely. The mixture was again stirred for 5 h at $10\text{--}20^{\circ}\text{C}$ until the white precipitate disappeared, then ice water (500 ml) was poured into the reaction mixture. A yellow crude product was formed and separated, and recrystallized with 95% ethanol to afford 44.1 g of **6** as light yellow crystals. Yield: 81%. m.p.: $127\text{--}127.5^{\circ}\text{C}$. IR (KBr): 3300($-\text{OH}$), 2250($\text{C}\equiv\text{C}$), 1560, 1510, 1430 (pyrimidine ring) cm^{-1} . ^1H NMR (CDCl_3) δ : 2.63 (s, 6 H, $-\text{CH}_3-\text{SCH}_3$), 4.43 ~ 4.53 (d, 2 H, $J = 5.0$ Hz, $-\text{CH}_2-$), 8.50 (s, 1 H). MS (EI, %) m/z : 219($\text{M}^+ + 1$, 95). Element analysis: Calculated for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{OS}$: C, 60.55; H, 4.59; N, 12.84; S, 14.68; Found: C, 60.49; H, 4.58; N, 12.80; S, 14.64.

2.6. 2,4-Pentadiyn-1-(*p-n,n*-dimethylaminoazobenzenesulfonate)-5-(*p*-methylthio-*o*-methylpyrimidine) (**7**)

A solution of **6** (2.18 g, 0.01 mol) in anhydrous tetrahydrofuran (30 ml) was cooled to 0°C , DABS-Cl (4.856 g, 0.015 mol) and sodium hydroxide solution (3 M, 10 ml) were added in turn with stirring. The mixture was stirred for 7 h at room temperature, after removing the precipitate formed from the reaction mixture by filtration; the solution was evaporated to dry with rotatory evaporator. The solid product was recrystallized from ethanol to give 3.03 g of **7** as a white solid. Yield: 60%. The product turned to red color when exposing to visible light. m.p.: $148\text{--}149^{\circ}\text{C}$. IR (KBr) 2850, 2200($\text{C}\equiv\text{C}$), 1590, 1570($\text{Ar}-$), 1550, 1500, 1400 (pyrimidine ring), 1350, 1170, 1120 ($-\text{C}-\text{O}-\text{C}-$), 920, 750 cm^{-1} . ^1H NMR ($\text{THF}-d_8$) δ : 2.40 (s, 3 H, $-\text{CH}_3$), 2.45 (s, 3 H, $-\text{SCH}_3$), 3.18 (s, 6 H, $-\text{N}(\text{CH}_3)_2$), 5.02 (s, 2 H), 6.86 ~ 7.80 (dd, 4 H, $J = 12.0$ Hz), 7.88 ~ 8.08 (dd, 4 H, $J = 12.0$ Hz), 8.40 (s, 1 H). MS (EI, %) m/z : 505(M^+ , 33), 506($\text{M}^+ + 1$, 100). Element analysis: Calculated for $\text{C}_{25}\text{H}_{23}\text{O}_3\text{N}_5\text{S}_2$: C, 59.41; H, 4.55; N, 13.86; S, 12.67; Found: C, 59.32; H, 4.69; N, 12.92; S, 12.61. UV-Vis (λ_{max} , THF): 455 nm.

2.7. Poly[2,4-pentadiyn-1-(*p-n,n*-dimethylaminoazobenzenesulfonate)-5-(*p*-methylthio-*o*-methylpyrimidine)] (**8**)

7 is susceptible to polymerization even at ambient temperature and in the dark in solid state, accompanying color change gradually from white to pale red, to deep red,

to purple red, as the polymerization process is going on. UV irradiation can accelerate this solid-state polymerization. As a light source, high-pressure mercury lamp was utilized. The conversion ratio of **7** to **8** was estimated by gravimetric method, since the monomer **7** has pretty good solubility in common organic solvents. The data of UV assistant polymerization of monomer **7** to polymer **8** is given in Table 1.

The conversion ratio was also confirmed by IR spectrum, through monitoring the intensity variation of the triple bond stretching vibration band.

DFWM technique was used to measure the macroscopic third-order susceptibility. The excitation was provided by 30 ps laser pulses at $\lambda = 532$ nm generated by Nd:YAG laser operating at 10 Hz repetition rate. Two of the wave are strong counterpropagating pump beams traveling in the forward and backward directions, and focused at the sample cell, and the wave diameter at sample was 0.5 mm. Their intensities satisfy the relation $I_1(z=0) = I_2(z=l)$ [7]. The third input wave was a weak probe beam ($I_3 = 10^{-2}I_1$) which made an angle of 5° with respect to the pump wave. CS_2 was used as a reference [8].

The microscopic third-order susceptibility γ was measured by z -scan technique. By measuring the intensity of transmission through the circular aperture behind the sample, the sign and the magnitude of n_2 can be determined [9]. The experimental curve was analyzed by the Gaussian decomposition method [10].

3. Results and discussion

Processibility is a key issue to be considered in diacetylene chemistry. A pyrimidine ring was designed and covalently bounded to the diacetylene chain successfully, the direct purpose is to improve solubility of the yielded diacetylene because of the presence of two nitrogen atoms in the pyrimidine ring. The electron-rich nitrogen atoms at the pyrimidine substituent will intensify the interaction between the diacetylene molecule and solvent and facilitate the dissolution process. In fact, **7** could be easily dissolved in common organic solvent, such as 1,2-dichloroethane, THF, acetone, and so on. On the other hand, in polymer **8**, the degree of π -electron conjugation is higher than usual diacetylene system because of the participating of the pyrimidine ring. Consequently, a large nonlinear optical activity is expected.

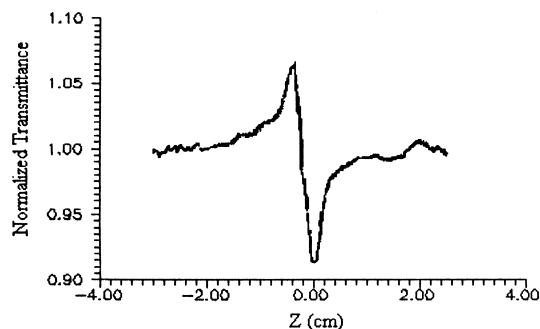
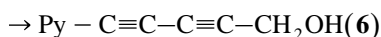
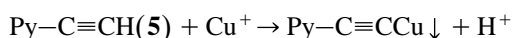


Fig. 1. Experimental z-scan curve of compound **8**.

To obtain unsymmetrical diacetylene **6** by Cadiot–Chodkiewicz coupling reaction according to the mechanism, a higher concentration of **5** has to be maintained in the reaction mixture, therefore, a slow adding of the alcohol has key importance or otherwise, the competitive self-coupling of the latter will occur.



where Py = pyrimidine.

The formation of cuprous precipitate with **5** has key importance. Similar to Glaser coupling reaction, hydroxylamine hydrochloride was needed to prevent from oxidizing of Cu^+ to Cu^{2+} , $n\text{-C}_4\text{H}_9\text{NH}_2$ was used to neutralize accompanying formed hydrohalogen acid, and to act as a ligand to form complex with diacetylene-cuprous precipitate to shift the reaction towards to right. However, amine such as ethylene diamine is not good, since it tends to form strong chelate directly with cuprous ion. In addition, the amount of amine added is also significant. The formation of amidine and amidino-oxine will occur when excess amount of amine is presented.

The polymerization rate of **7** is higher under similar conditions than other diacetylene derivatives, for example, higher than 2,4-hexadiyn-1,6-bis-(*p*-toluene-sulfonate) (PTS). By same gravimetric characterization method for estimation the degree of polymerization, most diacetylenes show much lower conversion ratio, while monomer **7** has 57% of conversion to polymer upon ultraviolet radiation. It is worthwhile to mention that the conversion ratio here only refers to the formation of highly polymerized polymer, but may not include those oligomers, which are still soluble in the solvent used.

DFWM and z-scan techniques were used for measuring the macro and microscopic susceptibilities $\chi^{(3)}$ and γ for the functionalized polydiacetylene **8**. $\chi^{(3)}$ was found to be 1.01×10^{-11} esu and γ equals to 1.06×10^{-30} esu. The experimental z-scan curve is shown in Fig. 1.

From the transmission curve in Fig. 1 and the corresponding position of the sample relative to the focus, the sign and the magnitude of the nonlinear refractive index n_2 of the sample was determined to be -1.18×10^{-11} esu.

In summary, a novel polydiacetylene with push–pull azobenzene chromophore attached as a side chain and a pyridine ring covalently bonded to the diacetylene conjugated system has been synthesized successfully with good yield. The diacetylene monomer is particularly interesting for its good processibility. The synthesis may be considered as an effective route to prepare soluble diacetylene derivatives by insertion of an electron-rich pyrimidine ring to such system. Preliminary measurements on third-order nonlinearity have been performed. Other possible applications of the synthesized material are undertaking.

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