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Synthesis and solid-state polymerization of 5-(*p*-methylthio-*o*-methyl-pyrimidinyl)-2,4-pentadiyn -1-ol and the third-order optical nonlinearity of its derivatives

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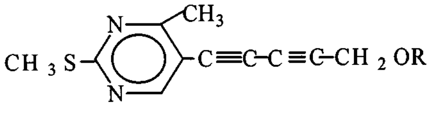
5-(*p*-Methylthio-*o*-methyl-pyrimidinyl)-2,4- pentadiyn -1-ol was synthesized by asymmetric couple method of Cadiot-Chodkiewicz and the mechanism of reaction was described. Several PDA's derivatives were obtained in good yields. These diacetylene monomers could easily dissolve in common organic solvents, and be polymerized thermally or under light illumination. Micro- and macroscopic third-order susceptibilities were measured by DFWM method for the yielded polymer. © *2000 Kluwer Academic Publishers*

1. Introduction

Polydiacetylenes are of particular interest for their large optical nonlinearities and fast excited-state relaxation times [1, 2]. its general formula (=CR-C≡C-CR=)*n* are 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 [3]. 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. pyrimidine ring with a methylthio group is such most effective and important chromophore. Only few publications about polydiacetylenes containing pyrimidine chromophore, especially about such soluble polymer, haven't appeared in the literature up to now [4]. In this paper, we reported the synthesis and characterization of diacetylene 5-(*p*-methylthio-*o*-methyl-pyrimidinyl)-2,4-pentadiyn-1-ol and its several derivatives, the structure of these monomers is shown below,



All the compounds studied in this work are presented in Table I. The general methodology for the synthesis of 5-(*p*-methylthio-*o*-methyl-pyrimidinyl)-2,4-pentadiyn-1-ol and its derivatives, and a possible mechanism of reaction for its several intermediates is shown in Scheme 1.

2. Experimental

FTIR spectra were obtained using a BIO-RAD FTS-165 IR spectrometer, and UV-visible absorption spectra were measured on UV-1601PC Shimadzu spectrophotometer. MS, ^{1}H-NMR and elemental analysis were measured on Trio-2000, Varian Gemini 300 operating at 300 MHz, and Heraeus CHN-RAPID instruments, respectively. Acetone and THF were distilled from sodium and benzophenone respectively. 1-methyl-α-pyrrolidone(NMP) was purifield by distillation over phosphorus pentoxidefrom and methanol over magnesium methoxide. *n*-butylamine, diisopropyl amine and triethylamine were further purified by distillation. They were stored in a drybox before use. Organic extracts were dried over Mg_2SO_4. All reactions were monitored by TLC prior to work-up. Solvents were removed with a rotary evaporator. TLC was run on silica plates 60 F254 (Merck) and visualised with UV fluorescence (254 and 366 nm) and/or molybdatophosphoric acid. The catalyst cuprous chloride is handled with dilute sulfuric acid for three times prior to use. S-Methyl-isothiourea sulfate **1** [5] was prepared following the procedure described in references.

2.1. Acetylacetonyl ethoxy methane (2)

A mixture of acetyl-acetone (100 g, 1.0 mol), triethyl orthoformate (260 g, 1.75 mol) and acetic anhydride

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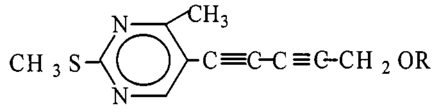
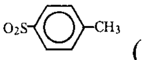
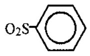
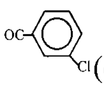
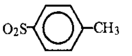
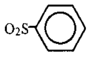
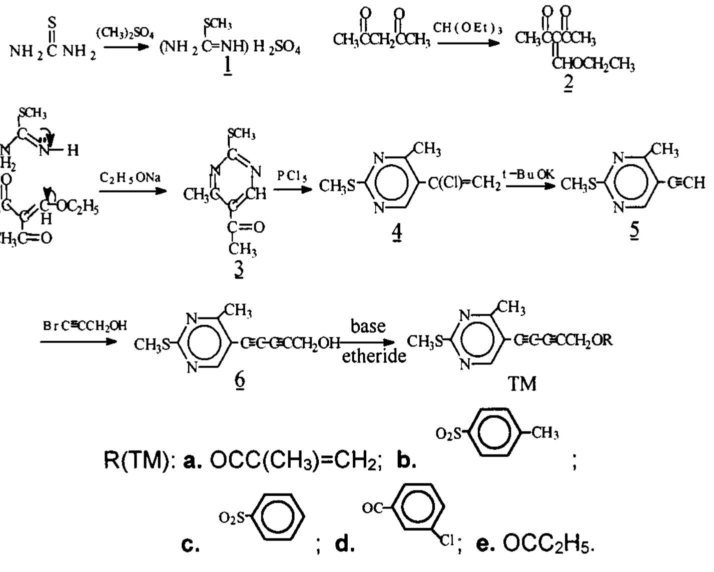
TABLE I The structure of PDA derivatives and $\chi^{(3)}$, γ value of their corresponding polydiacetylenes



R(Scheme 1)	$\chi^{(3)} \times 10^{-21}$ (V/m)^2 at $\lambda = 1064$ nm	$\gamma \times 10^{-42}$ (V/m)^2 at $\lambda = 1064$ nm	T ($=e^{-\alpha d}$)	λ_{max}/nm
$OCC(CH_3)=CH_2$(a)	5.480	25.902	1.000	307
 (b)	6.498	1.037	1.000	345
 (c)	6.923	8.054	1.000	348
 (d)	6.320	2.055	1.000	345
OCC_2H_5(e)	6.857	24.637	1.000	346
$ClCH_2CH_2Cl$(Solvent)	5.850	----		
	at $\lambda = 532$ nm	at $\lambda = 532$ nm		
$OCC(CH_3)=CH_2$(a)	177.513	16535.896	0.065	307
 (b)	12.377	1368.546	0.930	348
 (c)	7.548	1183.025	0.930	345
$ClCH_2CH_2Cl$(Solvent)	4.449	----		

note 1. The value here have included the contribution from the solvent. α is absorption coefficient(cm^{-1}), d is the thickness of sample pool ($d = 2$ mm).
2. T is transmissivity, including the reflection sample pool.



Scheme 1

(291 g, 2.84 mol) was refluxed with stirring for 3 h at 130°C. The solvent and unreacted acetic anhydride and triethyl orthoformate were removed, residue was distilled at 132–134°C/1.3 kPa to give light yellow liquid **2** (136 g, 87.5%). IR(KBr): 2 9 5 0 ($-CH_2-$, $-CH_3$), 1660 (-CO-) cm^{-1}. Anal. Calcd for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.31; H, 7.65.

2.2. 5-Acetyl-6-methyl-2-methylthiopyrimidine (3)

After sodium (25.3 g, 1.1 mol) was reacted completely with anhydrous ethyl alcohol (1×10^{-3}m^3), S-methylisothiourea sulfate **1** (139 g, 0.5 mol) and acetylacetonyl ethoxy methane **2** (156 g, 1.0 mol) were in turn added to the solution, and cooled to 0°C. The solution was stirred at room temperature for 1 h and then refluxed for 1 h. The Na_2SO_4 produced was hot filtered off and the filtrate was left for 24 h and filtered, the crude product was recrystallized with 95% ethyl alcohol to give a white solid **3** (127.5 g, 70%). m. p. 82–83°C. IR (KBr) 3000, 2900 (-CH_3), 1680(-CO-), 1510, 1400 (pyrimidine ring)cm^{-1}. Anal. Calcd for $C_8H_{10}N_2OS$: C, 52.74; H, 5.49; N, 15.39. Found: C, 52.58; H, 5.46; N, 15.30.

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

A solution of 5-acetyl-6-methyl-2-methylthio-pyrimidine **3** (91 g, 0.50 mol), phosphoric chloride (PCl_5)(125 g, 0.60 mol), and dry benzene (1.5×10^{-3} m^3) was refluxed for 3 h, and cooled to room temperature, then poured into cracked ice, neutralized with sodium carbonate saturated solution to $pH = 7$. The resulting mother liquor after extraction with benzene and evaporation of the solvent is distilled at 120–122°C/6.6 kPa to give clear liquid (**4**) (71 g, 71%). IR(KBr): 3000, 2950(-CH_3, =CH_2), 1620(-C=C-), 1550, 1500, 1400(pyrimidine ring)cm^{-1}. MS(EI, %) m/z: 201($M^+ + 1$). Anal. Calcd for $C_8H_9N_2SCl$: 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)

After a solution of 5-(1′-chloroethylene)-6-methyl-2-methylthio-pyrimidine **4** (100.3 g, 0.5 mol) in anhydrous ether (8×10^{-4} m^3) was cooled to 0°C, a t-BuOK/t-BuOH solution (1 M, 5.5×10^{-4} m^3) was added dropwise, the mixture was stirred for 4 h at room temperature. After evaporation of the solvent, the residue was distilled by water steam to afford a white solid (**5**) (59 g, 72%); m. p. 72–73°C. IR(KBr): 2100(C≡C), 1550, 1500, 1400(pyrimidine ring)cm^{-1}. MS(EI, %) m/z: 165($M^+ + 1$,98). Anal. Calcd for $C_8H_8N_2S$: 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)

After a mixture of cuprous chloride (1.0 g, 5 mmol), n-$C_4H_9NH_2$ (6×10^{-5} m^3) and THF/CH_3OH ($V:V = 1:1$, 4×10^{-4} m^3) under nitrogen was cooled to 0°C, hydroxyamine hydrochloride (20 g, 0.288 mol), and the compound **5** (41.0 g) was in turn added. After a while precipitate appeared, a solution of 3-bromopropargyl alcohol [6] (0. 35 mol) in THF/ CH_3OH($V:V = 1:1$, 1×10^{-4} m^3) was added dropwise. The mixture was again stirred for 5 h at 10–20 till the while precipitate disappeared, then poured into ice-water (5×10^{-4} m^3) and a yellow precipitate filtered was recrystallized with 95% ethanol to afford light yellow crystals **6** (44.1 g, 81%). m. p. 127–127.5°C. IR(KBr): 3300(-OH), 2250(C ≡ C) 1560, 1510, 1430(pyrimidine ring)cm^{-1}. ^1H NMR ($CDCl_3$): 2.63 (s, 6H, -CH_3- SCH_3), 4.43 ∼ 4.53 (d, 2H, $J = 5.0$ Hz, -CH_2-), 8.50 (s, 1H). MS(EI, %) m/z: 219($M^+ + 1$, 95). Anal. Calcd for $C_{11}H_{10}N_2OS$: 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-(ol-(-methylacrylate)-5-(p-methylthio-o-methyl-pyrimidine) (a)

1. α-Methylacrylic chloride: A mixture of (α-methylacrylic acid (1×10^{-4} m^3) and thionyl chloride ($SOCl_2$, 1×10^{-4} m^3) was refluxed for 2 h, light yellow liquor was distilled at 118°C/1.01 mPa to afford (α-Methylacrylic chloride as a colorless liquid (60 g). IR (KBr): 3450, 2930, 2890(-CH_2-, -CH_3), 1750(-CO-), 1610(-C=C-) cm^{-1}.

2. monomer **a**: A mixture of **6** (2.18 g, 0.01 mol), and α-methylacrylic chloride (6×10^{-6} m^3, 0.082 mol) in dry THF (3×10^{-5} m^3) was stirred for 4 h at room temperature and cooled to 0°C, and a solution of diisopropyl amine (6×10^{-6} m^3) in dry THF (1×10^{-5} m^3) was dropwised. The mixture is again stirred for 12 h at room temperature and poured into 2×10^{-4} m^3 ice-water, the precipitate was filtered off and dried. The crude product was recrystallized from n-hexane to afford a white crystal **a** (2.17 g, 76%). The product turned blue with exposure to visible light. m. p. 62°C. IR(KBr): 3000-2900(-CH_2-, -CH_3), 2200(-C≡C-), 1700(-CO-), 1620 (-C=C-), 1560, 1490, 1410, 1350(pyrimidine ring), 1150(-C-O-C-)cm^{-1}. ^1H NMR ($CDCl_3$): 1.90(s, 3H,-C=C-CH_3), 2.45 + 2.50(ss, 6H, pyrimidine -CH_3,-SCH_3), 4.82(s, 2H, -CH_2-), 5.54(s, 1H, -C=CH_2), 6.08(s, 1H, -C=CH_2), 8.37(s, 1H, pyrimidine -H). MS(EI, %) m/z: 286(M^+, 59), 69($M^+ - 217$, 100), 41(38). Anal. Calcd for $C_{15}H_{15}O_2N_2S_2$: C, 62.94; H, 4.90; N, 9.79; S, 11.8. Found: C, 62.75; H, 4.88; N, 9.76; S, 11.14. UV-vis (1,2-dichloroethane, monomer): 310 nm(λ_{max}), 337 nm(λ_{cutoff}). UV-vis (1,2-dichloroethane, Polydiacetylene): 451 nm(λ_{max}), 480 nm(λ_{cutoff}).

2.7. 2,4-Pentadiyn-1-(ol-tosyl)-5-(p-methylthio-o-methyl-pyrimidine) (b)

A mixture of **6** (21. g, 0.1 mol), and tosyl chloride (28.6 g, 0.15 mol) in dry THF (3×10^{-4} m^3) was cooled to 0°C with stirring, and a solution of sodium hydroxide (13.2 g, 0.3 mol) in water (1×10^{-4} m^3) was dropwised. The mixture is again stirred for 7 h at room temperature, filtered, and the filtrate was poured into 5×10^{-4} m^3 ice-water, the precipitate was filtered off and dried. The crude product was recrystallized from 95% ethyl alcohol to give a brown yellow crystal **b** (30.0 g, 80%). The product turned pink with exposure to visible light, m. p. 114–114.5°C. IR(KBr): 2250(-C≡C-), 1560, 1490, 1410, 1350(pyrimidine ring), 1200, 1150(-C-O-C-), 950, 765, 710 cm^{-1}. ^1H NMR ($CDCl_3$): 2.40(s, 3H, -CH_3), 2.56 (s, 3H, pyrimidine -CH_3), 2.61(s, 3H, -SCH_3), 4.80(s, 2H, -CH_2-), 7.20–7.82(dd, 4H, -Ar), 8.34(s, 1H, pyrimidine H). MS(EI, %) m/z: 373($M^+ + 1$, 73), 201 (100), 173(48). Anal. Calcd for $C_{18}H_{16}N_2O_3S_2$: C, 58.06; H, 4.30; N, 7.53; S, 17.2. Found: C, 58.00; H, 4.28; N, 7.55; S, 17.14.

2.8. 2,4-Pentadiyn-1-(ol-phenylsulfonyl)-5-(*p*-methylthio-o-methyl-pyrimidine) (c)

A solution of **6** (2.2 g, 0.01 mol), and phenylsulfonyl chloride (1.5×10^{-6} m^3, 0.012 mol) in dry THF (5×10^{-5} m^3) was stirred for 24 h at room temperature, and then cooled to 0°C, a solution of potassium hydroxide (1.12 g, 0.02 mol) in water (1×10^{-5} m^3) was dropwised. The mixture is again stirred for 7 h at room temperature, and poured into 5×10^{-4} m^3 ice-water, the yellow precipitate was filtered off and dried. The crude product was recrystallized from 95% ethyl alcohol to give a brown yellow crystal **c** (3.2 g, 90%). m. p. 89–90°C. IR(KBr): 2900–3050 (-CH$_2$-, -CH$_3$), 2250(-C≡C-), 1560, 1510, 1430(pyrimidine ring), 1180(-C-O-C-), 950, 780, 740 cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.40(*s*, 3H, -CH$_3$), 2.56(*s*, 3H, pyrimidine -CH$_3$), 2.61(*s*, 3H, -SCH$_3$), 4.80(*s*, 2H, -CH$_2$-), 7.20 ~ 7.82(*dd*, 4H, -Ar), 8.34(*s*, 1H, pyrimidine H). MS(EI, %) *m*/*z*: 358(M$^+$, 48), 201(30), 78(100). Anal. Calcd for $C_{17}H_{14}N_2O_3S_2$: C, 56.98; H, 3.91; N, 7.82; S, 17.88. Found: C, 57.00; H, 3.92; N, 7.80; S, 17.78.

2.9. 2,4-Pentadiyn-1-(ol-*m*-chlorobenzoyl)-5-(*p*-methylthio-*o*-methyl-pyrimidine) (d)

1. *m*-Chlorobenzoyl chloride: A mixture of *m*-chlorobenzoic acid (8 g) and thionyl chloride (1×10^{-4} m^3) was refluxed with stirring for 4.5 h to obtain a red brownish solution, the crude product was directly used for next reaction.

2. **d**: A solution of **6** (1.5 g), and *m*-chlorobenzoyl chloride (1.5×10^{-6} m^3) in dry THF (2.5×10^{-5} m^3) was stirred for 8 h at room temperature and a white crystals was produced, continuing to stir for 14 h and the mixture was poured into water (4×10^{-4} m^3), and neutralized to PH = 7 with sodium hydroxide, a brown yellow precipitate was produced and filtered, dried, recrystalized with *n*-hexane to afford a light yellow crystals **d** (1.7 g, 70%). m. p. 77–78°C. IR(KBr): 2590(-CH$_2$-, -CH$_3$), 2250(-C≡C-), 1720(-CO-), 1560, 1500, 1410, 1350(pyrimidine ring) cm^{-1}. ^{1}H NMR(CCl$_4$): 2.47(*s*, 3H, -SCH$_3$), 2.53(*s*, 3H, pyrimidine -CH$_3$), 5.00(*s*, 2H, -CH$_2$-), 7.42 ~ 7.97(*m*, 4H, -Ar), 8.37(*s*, 1H, pyrimidine -H). MS(EI, %) *m*/*z*: 356(M$^+$, 37), 139(M$^+$ − 117, 100), 87(58). Anal. Calcd for $C_{18}H_{13}O_2N_2SCl$: C, 60.59; H, 3.65; N, 7.85; S, 8.98. Found: C, 60.57; H, 3.65; N, 7.80; S, 8.95.

2.10. 2,4-Pentadiyn-1-(ol-propionate)-5-(*p*-methylthio-*o*-methyl-pyrimidine) (e)

A solution of **6** (0.8 g), and propionyl chloride (3×10^{-6} m^3) in dry THF (3.5×10^{-5} m^3) was stirred for 10 h at room temperature, then cooled to 0°C, and triethylamine was added dropwise and a white crystals was produced. After stirring for 5 h again and the mixture was poured into water (4×10^{-4} m^3), a yellow precipitate was produced and filtered, dried, recrystalized with ethyl alcohol to obtain yellow crystals **e** (0.7 g, 70%). m. p. 78–79°C. IR(KBr): 3000 ~ 2900(-CH$_2$-, -CH$_3$), 2250(-C≡C-), 1740(-CO-), 1560, 1490, 1410, 1350(pyrimidine ring) cm^{-1}. 1H NMR(CCl$_4$): 1.23(*t*, 3H, $J = 5.0$ Hz), 2.12–2.46(*q*, 2H, -OCO-CH$_2$-), 2.56(*s*, 3H, pyrimidine -CH$_3$), 2.61(*s*, 3H, -SCH$_3$), 4.81(*s*, 2H, -CH$_2$-), 8.10(*s*, 1H, pyrimidine -H). MS(EI, %) *m*/*z*: 274(M$^+$, 54), 218(M$^+$ − 56, 60), 87(58), 56(100), 29(70). Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.31; H, 5.11; N, 10.22; S, 11.68. Found: C, 61.40; H, 5.10; N, 10.17; S, 11.63.

2.11. Solid-State Polymerization

The monomer **a**, **b**, **c** were polymerized by heating the crystals in a vacuum vessel below the melting point or γ-ray or UV irradiation of the crystals at room temperature. ^{60}Co γ-ray with the dose rate 0.1 Mrad/h or a high-pressure mercury lamp (200 W) was used for the polymerization. Polymer conversion was determined by extraction of residual monomer with ethanol. Time-conversion curves of the thermal polymerization of monomer **b**, **c** at 95°C were shown in Fig. 4.

2.12. Preparation of polydiacetylene thin films

To a 25 ml three-neck round bottom flask were added diacetylene monomer **a** (26.60 mg, 0.093 mmol) and NMP (5 mL) under nitrogen atmosphere. The solution was stirred for 20 min and the poly(methyl methacrylate)(PMMA) (21.05 mg, 0.217 mmol) (monomer **a**/PMMA = 3 : 7(mol)) was then added at 0°C. The mixture was stirred at 0°C for 3 h and at room temperature for another 48 h under nitrogen atmosphere. The resulting solution was filtered through a 0.2 μm Teflon filter and was spin-coated onto normal glass slides. The films were dried for 16 h in a vacuum at room temperature, and the temperature was increased to 95 for 48–72 h under nitrogen atmosphere. The thickness of blue films were measured by a *alpha-step 250 TENCOR* instrument, and found to be varied from 1.0–1.8 μm, depending on the precuring time and the spin rate.

2.13. Measurement of third-order NLO properties

DFWM technique was used to measure the macroscopic third-order susceptibility. The excitation was provided by **8** ns 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].

As a function of the laser intensity, the relative intensity of the DFWM signal are plotted in Fig. 1,

The slope of the straight line in Fig. 1 is 2.87 which indicates that the relationship between the signal intensity I_s and the input power I is consistent with

$$I_s = A\left(\frac{f\chi^{(3)}}{n_0^2}\right)^2 I^3 \qquad (1)$$

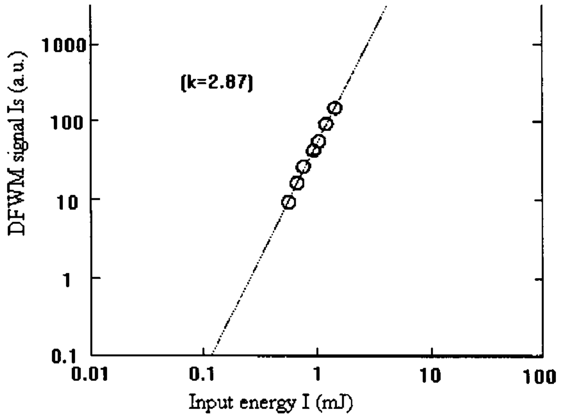


Figure 1 Measured DFWM signal intensity I_s dependences of laser intensity I at 1.064 μm for polymer **a** in dichloromethane.

where A is a constant, depending on the beam path length and absorptance of a sample, and alignment of the beams; f represents the volume fraction of the sample to solution, n_0 is linear refractive index of the sample. $\chi^{(3)}$ $(=\chi^{(3)}_{xxxx})$ for polymer **a** is 177.513 × 10^{-21} $(\mathrm{V/m})^2(\lambda = 0.530\ \mu\mathrm{m})$ calculating with Equation 1.

Due to the contribution of the tensor $\chi^{(3)}_{xyyx}$ in orthogonal polarization conditions, DFWM signals of the sample and reference solution were measured as follows,

$$\left(\frac{I_s}{I_r}\right)_{xyyx} = \left(\frac{I_s}{I_r}\right)_{xxxx} \qquad (2)$$

where I_s and I_r are intensities of the sample and reference solution respectively. Equation (6) indicates that $\chi^{(3)}_{xxxx}$ and $\chi^{(3)}_{xyyx}$ for the sample is the same as that for CS_2 [9].

3. Results and discussion

To obtain unsymmetrical diacetylene **6** by Cadiot-Chodkiewicz coupling reaction [10] according to the mechanism, a higher concentration of compound **5** has to be maintained in the reaction mixture, therefore, a slow adding of the 3-bromopropargyl alcohol and the formation of cuprous precipitate with **5** have key importance owing to otherwise the competitive self-coupling of the later will occur,

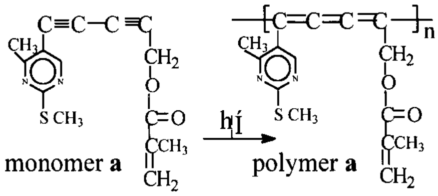
$$\begin{aligned} &\mathrm{Py\,C{\equiv}CH} + \mathrm{Cu}^+ \rightarrow \mathrm{Py\,C{\equiv}CCu}\downarrow + \mathrm{H}^+ \\ &\mathrm{Py\,C{\equiv}CCu} + \mathrm{HOCH_2C{\equiv}CBr} \\ \rightarrow\ &\mathrm{Py\,C{\equiv}C{-}C{\equiv}C{-}CH_2OH} \qquad (3) \\ &(\mathrm{py} = \text{pyrimidine ring}) \end{aligned}$$

Similar to Glaser coupling reaction, hydroxyamine hydrochloride was needed to prevent from oxidizing of Cu^+ to Cu^{2+}, n-$C_4H_9NH_2$ was used to neutralize accompaning 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 ammount of amine is presenting.

$$\mathrm{ArC{\equiv}CBr} \xrightarrow[\substack{\mathrm{N\,H_2OHHCl} \\ \mathrm{CuCl}}]{n\text{-}\mathrm{BuN\,H_2/EtOH}} \mathrm{ArCH_2C(NHBu){=}(Bu)}$$

$$+\,\mathrm{ArCH_2C(N\,HBu){=}NOH} \qquad (4)$$

Processibility is a key issue to be considered in diacetylene chemistry. A pyrimidine ring was designed and be 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, diacetylenes monomers synthesized could be easily dissolved in common organic solvent, such as 1,2-dichloroethane, tetrahydrofuran, acetone, and so on. On the other hand, in its polymer, the degree of π-electron conjugation is higher than usual diacetylene system (for example monomer **a**, Scheme 2) because of the participating of the pyrimidine ring. Consequently, a large nonlinear optical activity is expected.



Scheme 2

In fact, compound **a** is susceptible to polymerization even at ambient temperature and in the dark in solid state. At the initial stage of the polymerizations, a white needle-typed crystals of **a** became purple with metallic luster and further did purple black by γ-irradiation. By γ-ray irradiation with 0.1 Mrad/h dose rate, the conversion ratio of **a** monomer to its corresponding polydiacetylene was estimated by gravimetrical method, it took 480 h to reach 68% conversion. This may simply be because the polymer formed near the crystal surface absorbs γ-ray. some other reasons, like quenching of excited monomers [11], have been proposed for this kind of saturation. The curves of γ assistant polymerization of monomer **a** to its corresponding polydiacetylene is given in Fig. 2.

This transmission spectra were obtained with the thin film, ca. 1.0 μm thick of **a**/PMMA on a glass plate. The monomer **a** polymerized very fast with UV irradiation at room temperature. Transmission maximum of monomer **a** exists at 345 nm, whereas that of UV-irradiate 30 minutes is 480 nm, shown in Fig. 3. Time conversion curves of monomer **b**, **c** thermal polymerization at 95°C are also shown in Fig. 4, where the polymer conversion was determined by IR absorption intensity of triple bond stretching vibration in comparison with that pyrimidine carbon skeleton. Since two triple bond stretching vibrations decreased in the same

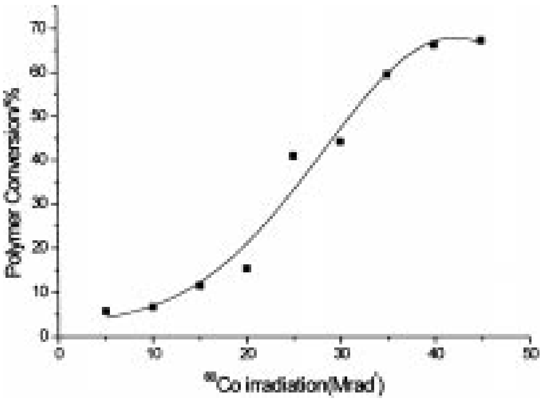


Figure 2 Mrad-conversion curves of ^{60}Co γ-ray polymerization of monomer **a**: (—) modification. *0.1 Mrad/h

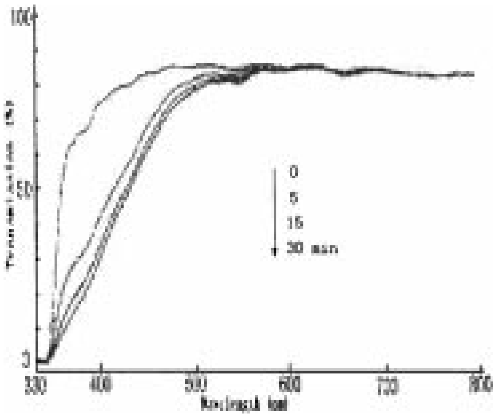


Figure 3 UV-Visible transmission spectrum changes of monomer **a**. The transmission spectra from up to down are one of 0, 5, 15, 30 minutes with UV irradiation, respectively.

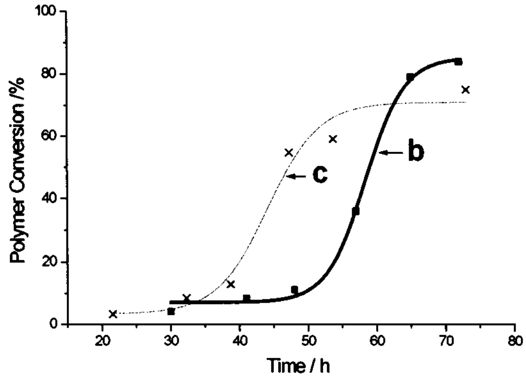
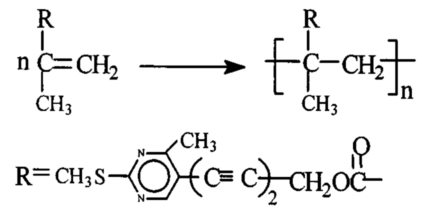


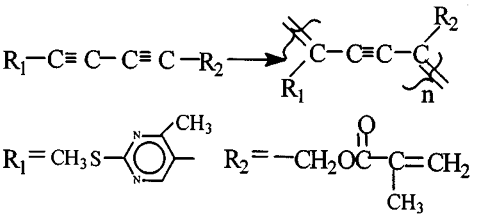
Figure 4 Time-conversion curves of the thermal polymerization of monomer **b**, **c** at 95°C: (—) modification **b**; (---) modification **c**.

proportion, it is obvious that the polymerization proceeds by 1,4-addition. As seen from Fig. 4, both modifications reached 85% **(b)**, 69%**(c)** conversions via thermal polymerization respectively.

Owing to there are diacetylene and ethenoid two active groups in compound **a**, it is important which group has polymerized when γ-ray irradiate the crystals at room temperature. In fact, it was diacetylene that has polymerized because i) the solid-state polymerization of diacetylene as often as not posses metallic luster, and polymer **a** has purple metallic luster. ii) if ethene group is polymerized the structure of the molecule **a** would happen large changes (5), Two ethene hytrogens peak at 6.08 and 5.54 ppm would disappeared and appeared ethane hydrogens peak at 2–3 ppm in ^{1}H-NMR of the polymer as compared with one of corresponding monomer; if diacetylene is polymerized the structure of the monomer molecule would similar to one of polymer (6). In fact, the structure of monomer **a** has little different from one of the polymer **a** in their ^{1}H-NMRs.



(5)



(6)

Table I lists the data obtained from the DFWM experiments. For polymer **a**, the three-order nonlinear optical susceptibility $\chi^{(3)}$ is 5.480×10^{-21} (V/m)^2 ($\lambda = 1064$ nm, $c = 1.78 \times 10^{-3}$ M, $T = e^{-\alpha d} = 1.000$), corresponding the value of γ is 25.092×10^{-42} (V/m)^2; at $\lambda = 532$ nm the value of $\chi^{(3)}$ is 177.513×10^{-21} (V/m)^2 ($c = 1.78 \times 10^{-3}$ M, $T = e^{-\alpha d} = 0.065$), corresponding the value of γ is $16535.896 \times 10^{-42}$ (V/m)^2. Polymer **a** showed very large second-order hyperpolarizability γ, its magnitude ($\lambda = 532$ nm) is 10^{-38} (V/m)^2 level, coming close to the maximum (10^{-37} (V/m)^2) presented in the literature [12]. Though the magnitude measured have partly resonance enhancement ($T = 0.065$), this is also abnormal compared with the other PAD derivatives.

In conclusion we have disclosed an efficient preparation of 5-(p-methylthio-o-methyl-5-pyrimidinyl) 2, 4-pentadiyn-1-ol under smooth conditions in good yields and obtained corresponding some novel diacetylene monomers with ester alkyl/phenylsulfonyl attached as a side chain. The diacetylenes monomer is particularly interesting for theirs good processibility. Preliminary measurements on third-order nonlinearity have been performed. The linear index of the refraction of polymer **a** and high quality channel waveguide formed by Ag$^+$ – Na$^+$ exchange method, and the transmission of complex waveguide will be published elsewhere.

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