Synthesis and solid-state polymerization of 5-(2-methylthio-4-methylpyrimidin-5-yl)penta-2,4-diyn-1-ol and of several of its derivatives

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5-(2-Methylthio-4-methylpyrimidin-5-yl)penta-2,4-diyn-1-ol was synthesized by asymmetric coupling, and the corresponding diacetylene monomers were also prepared in good yields. These monomers could be dissolved in common organic solvents. The monomers can be polymerized in the solid state using heat, light or γ-radiation. In addition, micro- and macroscopic third-order susceptibilities were measured by the degenerate four-wave mixing (DFWM) method for the yielded polymers.

Introduction

Polydiacetylenes are of particular interest for their large optical nonlinearities and fast response speed.[1,2] As optical materials, they frequently have to be made as films, and therefore their processability is of key importance for successful optical application. Unfortunately, this is a particular problem with diacetylene compounds. For this reason, we designed a pyrimidine ring with two substituents and combined it directly with the diacetylene carbon backbone in order to improve its solubility. The nitrogen atoms in pyrimidine can improve the interaction between the diacetylene and solvent molecules, and thus facilitate solution of the diacetylene. Furthermore, an ester substituent was also introduced to the other side of the diacetylene molecule for the same purpose. For example, the methacrylate group attached to the diacetylene monomer **7a** participates in the Van der Waals interactions between the monomer and solvent molecules, and therefore facilitates the material's processing. The modifications of the chemical structures of the diacetylene molecule described above allow the yielded polydiacetylene materials to be prepared in the form of thin films or in solution. In fact, the diacetylene monomers synthesized in this work could be easily dissolved in common organic solvents, such as 1,2-dichloroethane, tetrahydrofuran and acetone. In addition, in their corresponding polymers, the degree of π-electron conjugation is higher than in conventional diacetylene systems because of the participation of the pyrimidine ring. Consequently, a higher nonlinear optical activity is expected.

Only a few publications on polydiacetylenes containing the pyrimidine chromophore have appeared in the literature up to now.[3,4] In this paper, we report the synthesis and characterization of the diacetylene 5-(2-methylthio-4-methylpyrimidin-5-yl)penta-2,4-diyn-1-ol and of several of its derivatives. The general methodology for the synthesis and a possible mechanism for the formation of the related intermediates are shown in Scheme 1.

Results and discussion

1. Formation of diacetylene 6

The unsymmetrical diacetylene **6** was obtained by a Cadiot–Chodkiewicz coupling reaction[4] according to the mechanism shown below [eqn. (1)]. The formation of the copper complex

$$\underset{\mathbf{5}}{\mathrm{PyC{\equiv}CH}} + \mathrm{Cu^{+}} \longrightarrow \mathrm{PyC{\equiv}CCu{\downarrow}} + \mathrm{H^{+}}$$

$$\mathrm{PyC{\equiv}CCu + HOCH_2C{\equiv}CBr} \longrightarrow \underset{\mathbf{6}}{\mathrm{PyC{\equiv}C{-}C{\equiv}C{-}CH_2OH}} \quad (1)$$

(Py = pyrimidine ring)

of **5** is a key step and 3-bromopropargyl alcohol (3-bromoprop-2-ynyl alcohol) was added dropwise to avoid the possible self-coupling reaction of 3-bromopropargyl alcohol.

As in the Glaser coupling reaction, amine is needed to prevent the oxidation of Cu^{+} to Cu^{2+}, to neutralize the concomitantly formed hydrohalogen acid, and to act as a ligand to form a complex with the diacetylene–cuprous ion precipitate, driving the reaction forwards. However, ethylenediamine is not a good ligand since it tends to form a strong chelate complex directly with the cuprous ion, and so *n*-butylamine is more appropriate. Addition of the correct amount of amine is also significant, as the formation of amidine and amide oxime will occur when excess amine is present, as shown in eqn. (2).

$$\mathrm{ArC{\equiv}CBr} \xrightarrow[\substack{\mathrm{NH_2OHHCl}\\ \mathrm{CuCl}}]{n\mathrm{BuNH_2{-}EtOH}} \mathrm{ArCH_2C(NHBu){=}(NBu)} + \mathrm{ArCH_2C(NHBu){=}NOH} \quad (2)$$

2. Solid-state polymerization

Compound **7a** is readily polymerized in the solid state by means of ^{60}Co γ-ray or UV irradiation even at ambient temperature (Scheme 2). Under ^{60}Co γ-ray irradiation, the white needle-shaped crystals of **7a** became purple with a metallic luster, and then turned to purple–black. With a dose rate of 0.1 Mrad h^{-1} it took 480 h to reach 68% conversion, as estimated by gravimetry. This may be because the polymers formed at the surface prevent the underlying monomers from polymerizing further. Other reasons, such as the quenching of excited monomers, have been proposed for this kind of saturation.[5] The results of γ-ray assisted polymerization of **7a** to its corresponding polydiacetylene are given in Table 1. Further information could also be gained from a crystal structure determination of the polymer.

The UV-induced polymerization of **7a** was monitored by its transmission spectrum, as shown in Fig. 1.

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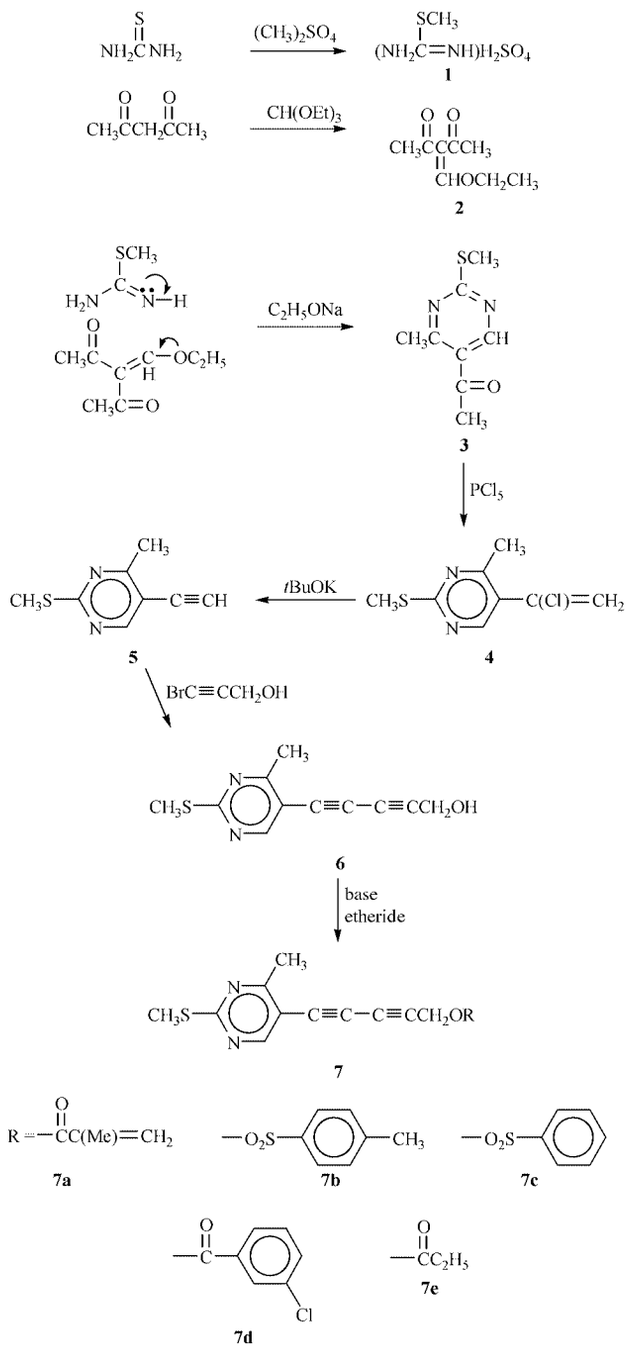
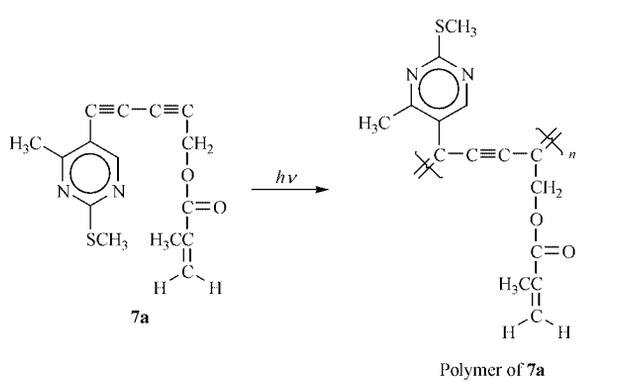


Scheme 1



Scheme 2

The transmission spectra of **7a** and of its corresponding polymers were obtained from a 1.0 μm thin film of the poly(methyl methacrylate) PMMA polymer doped with **7a**. Transmission decreased during irradiation at room temperature,

Table 1 Solid-state polymerization of **7a** by ^{60}Co γ-ray irradiation

^{60}Co irradiation dose/Mrad[a]	**7a**/g	Polymer/g	Conversion ratio (%)
5	0.4366	0.0252	5.77
10	0.4834	0.0325	6.73
15	0.5001	0.0577	11.54
20	0.4985	0.0767	15.38
25	0.4937	0.2022	40.96
30	0.4883	0.2160	44.23
35	0.4758	0.2837	59.62
40	0.4770	0.3165	66.35
45	0.4932	0.3320	67.31
48	0.4687	0.3200	68.27

[a] Irradiation at a rate of 0.1 Mrad h^{-1}.

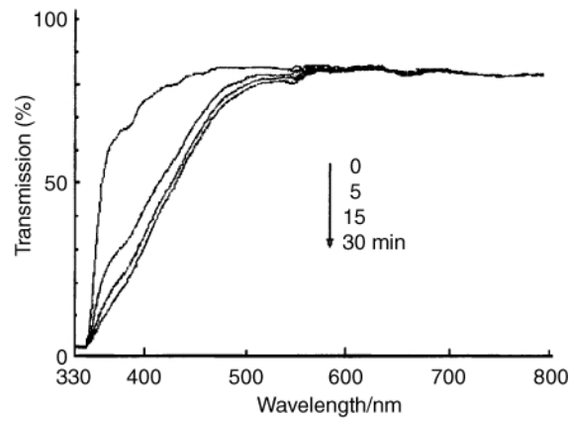


Fig. 1 Variation of the UV–visible transmission spectra of **7a** under UV irradiation. The transmission spectra were obtained from top to bottom after 0, 5, 15 and 30 minutes irradiation, respectively.

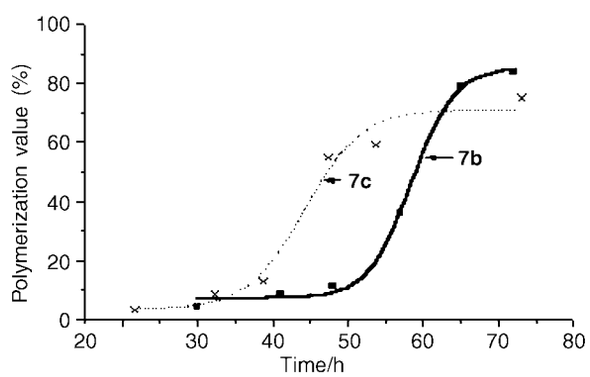


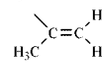
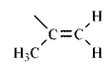
Fig. 2 Time–conversion curves of **7b** and **7c** during the thermal polymerization reaction at 95 °C.

as shown clearly in Fig. 1, which indicates that solid-state polymerization has occurred in **7a** and that the degree of π-electron conjugation is increased greatly during the polymerization process. Nevertheless, under UV irradiation, even at ambient temperature, the efficiency of the polymerization, as indicated in Fig. 7, was not as good.

Time–conversion curves for thermal polymerization of **7b** and **7c** at 95 °C are shown in Fig. 2, where the polymerization value was determined by the IR absorption intensity of the triple-bond stretching vibration in comparison with that of the pyrimidine carbon skeleton. Since the intensities of the two triple-bond stretching vibrations decreased in the same proportion, it is obvious that the polymerization proceeds by 1,4-addition.[6] As shown in Fig. 2, thermal polymerization values of 85 and 69% have been reached for **7b** and **7c**, respectively.

Owing to the presence of two active groups, *i.e.* the diacetylene and ethylene groups, in **7a**, it is important to know which group was genuinely active in the polymerization under γ-ray

Table 2 Assignments for the ^{1}H NMR spectrum of the polymer of **7a** in $CDCl_3$ (300 MHz)

Chemical shifts δ (ppm)	Multiplicity	J/Hz	Integration values	Assignment
8.457	s	—	0.8883	Pyrimidine H
6.181–6.174	m	0.9, 1.2	0.9279	
5.643–5.627	m	1.5, 1.5, 1.8	0.9415	
4.896	s	—	1.9526	$-CH_2-$
2.550	s	—	3.0000	$-SCH_3$
2.544	s	—	3.0927	Pyrimidine $-CH_3$
1.962–1.954	dd	1.2, 1.2	3.0000	Ethylene $-CH_3$
7.240	s	—	—	—

[a] See Scheme 2 for numbering.

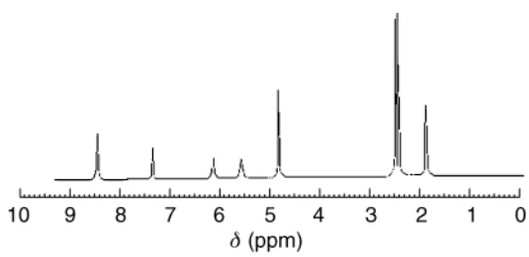


Fig. 3 ^{1}H NMR spectrum of **7a** in CCl_4 (60 MHz).

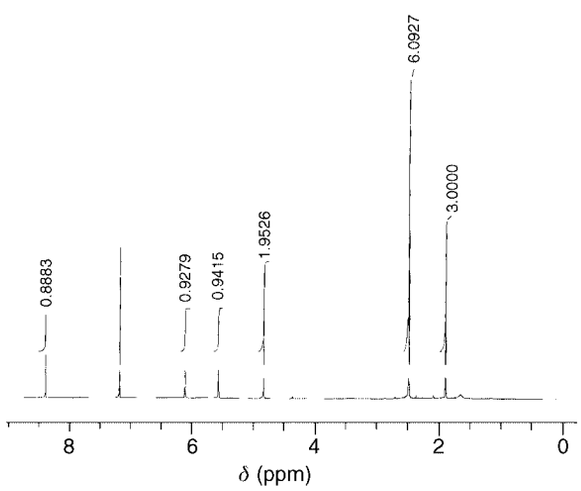


Fig. 4 ^{1}H NMR spectrum of the polymer of **7a** in $CDCl_3$ (300 MHz).

irradiation. The observations supporting the polymerization of the diacetylene group are as follows: i) the solid-state polymerization of ethene does not usually produce polymers with a metallic luster, but diacetylenes do; ii) if the ethene group is polymerized, two ethylene hydrogen peaks at 6.19 and 5.64 ppm would disappear and a single peak for $-CH_2-$ at 2–3 ppm would arise. If the diacetylene group is polymerized, the ^{1}H NMR spectrum of the **7a** polymer would be similar to that of the **7a** monomer, as the chemical shifts of two hydrogen peaks at 6.19 and 5.64 ppm would not change greatly and this concurs with our observations (see Figs. 3 and 4; the assignment of the peaks and integration values are shown in Table 2).

3. Raman spectrum of polymeric 7a

The FT-Raman spectrum of the polymer of **7a** is given in Fig. 5. There are two strong peaks at 2087 and 1460 cm^{-1} which can be assigned to the C≡C and C=C stretching vibrations of the polydiacetylene backbone, respectively. A similar diacetylene monomer, 8-[(butoxycarbonyl)methyl]urethanyl-1-(5-pyrimidyl)-octa-1,3-diyne (BPOD), shows vibrational bands at 2245–2221 (C≡C stretch) and 1570 cm^{-1} (C=C stretch of the

Table 3 The third-order optical nonlinear susceptibilities, $\chi^{(3)}$, and γ values of the monomer **7** and of its corresponding polymers

Compound	$\chi^{(3)}/10^{-13}$ esu	$\gamma/10^{-34}$ esu	T^a (= e^{-ad})	λ_{max}/nm
λ = 1064 nm				
Polymer of **7a**	3.925	17.974	1.000	307
Polymer of **7b**	4.655	0.743	1.000	345
Polymer of **7c**	4.959	5.770	1.000	348
Polymer of **7d**	4.527	1.472	1.000	345
Polymer of **7e**	4.912	17.648	1.000	346
$ClCH_2CH_2Cl$ (solvent)	4.191	—		
λ = 532 nm				
Polymer of **7a**	127.158	11845.198	0.065	307
Polymer of **7b**	8.866	980.334	0.930	348
Polymer of **7c**	5.407	847.439	0.930	345
$ClCH_2CH_2Cl$ (solvent)	3.187	—		

[a] T is transmissivity, including the reflection of the UV cell. The values incude the contribution from the solvent, a is absorption coefficient (cm^{-1}), d is the thickness of the UV cell (d = 2 mm).

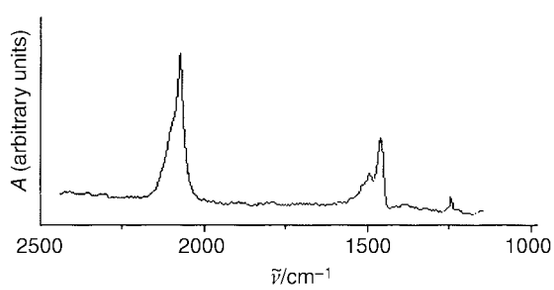


Fig. 5 Principal Raman vibrational bands of polymeric **7a**.

aromatic ring) in its Raman spectrum.[4b] The relative Raman shifts of the polymer of **7a** when compared with those of BPOD implies a more asymmetric character of the polymeric **7a** macromolecule as evidenced by the increase in the energy of the C≡C and C=C stretching movements in the polymer backbone. The spectrum in Fig. 5 presents evidence for a vinylic backbone structure and also the shift at 1500 cm^{-1} suggests the presence of two different species; the triple bond shift is sufficiently broad to include more than one shifted line.

4. Micro- and macroscopic third-order susceptibilities

The third-order optical nonlinear properties of the synthesized materials were also examined. The data obtained by the DFWM method are given in Table 3.

As indicated in Table 3, the $\chi^{(3)}$ and γ values of polymer **7a** at 532 nm are quite large and are more than 30 times greater for

$\chi^{(3)}$ and about 650 times bigger for the γ values compared with the corresponding values at 1064 nm. Although the exceptionally large values partly come from a resonance enhancement contribution ($T = 0.065$), this is also abnormal in comparison with those of the other polydiacetylene polymers.

In conclusion, we have disclosed an efficient approach for preparing 5-(2-methylthio-4-methylpyrimidin-5-yl)penta-2,4-diyn-1-ol under smooth conditions in good yields and obtained some novel diacetylene monomers with alkoxycarbonyl and phenylsulfonyl side chains. The diacetylene monomers are interesting because of their good processability. Experimental results demonstrate that polymeric **7a** displays a large third-order optical nonlinearity. The refractive index of polymeric **7a** and its channel waveguide formed by the Ag^+–Na^+ ion-exchange method, and the waveguide characters will be published elsewhere.

Experimental

FT-IR spectra were obtained using a Bio-Rad FTS-165 IR spectrometer. UV-vis absorption spectra were measured with a Shimadzu UV-1601PC spectrophotometer. Mass spectra were recorded on a Trio-2000 spectrometer, and elemental analysis was made on a Heraeus CHN-Rapid instrument. ^{1}H NMR spectra were taken on a Varian Gemini 300 spectrometer operating at 300 MHz. 1-Methyl-α-pyrrolidone (NMP) was purified by distillation over phosphorus pentaoxide. Methanol was purified by distillation over magnesium methoxide. *n*-Butylamine, diisopropylamine and triethylamine were purified by distillation and stored in a dry-box before use. All reactions were monitored by TLC prior to work-up. Solvents were removed with a rotary evaporator. TLC was run on silica plates GF254 and the developed plate was visualized with UV fluorescence ($\lambda = 254$ and 366 nm). The catalyst cuprous chloride was washed with dilute sulfuric acid three times prior to use. *S*-Methylisothiourea sulfate **1** was synthesized according to the literature method.[7]

1-Acetylaceton-1-ylidene(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 3 h at 130 °C. The solvent and unreacted acetic anhydride and triethyl orthoformate were removed and the residue was vacuum distilled at 132–134 °C/1.3 kPa to give a light yellow liquid **2** (136 g, 87.5%). IR (KBr): ν 2950 (–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%.

5-Acetyl-4-methyl-2-methylthiopyrimidine 3

Sodium (25.3 g, 1.1 mol) was reacted completely with anhydrous ethyl alcohol (1000 ml), after which *S*-methylisothiourea sulfate **1** (139 g, 0.5 mol) and 1-acetylaceton-1-ylidene(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 filtered off while still hot, 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%). Mp 82–83 °C. IR (KBr): ν 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%.

5-(1′-Chlorovinyl)-4-methyl-2-methylthiopyrimidine 4

A solution of 5-acetyl-4-methyl-2-methylthiopyrimidine **3** (91 g, 0.50 mol), phosphorus pentachloride (PCl_5) (125 g, 0.60 mol), and dry benzene (1500 ml) was refluxed for 3 h, and cooled to room temperature, then poured into cracked ice and a saturated solution of sodium carbonate was added until pH 7 was reached. After extraction with benzene and evaporation of the solvent the resulting mother liquor was distilled at 120–122 °C/6.6 kPa to give clear liquid **4** (71 g, 71%). IR (KBr): ν 3000, 2950 (–CH_3, =CH_2), 1620 (–C=C–), 1550, 1500, 1400 (pyrimidine ring) cm^{-1}. MS (EI) *m*/*z*: 201 ($M^+ + 1$, 71%). 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%.

5-Ethynyl-4-methyl-2-methylthiopyrimidine 5

After a solution of 5-(1′-chlorovinyl)-4-methyl-2-methylthiopyrimidine **4** (100.3 g, 0.5 mol) in anhydrous ether (800 ml) had been cooled to 0 °C, a solution of *t*BuOK–*t*BuOH (1 M, 550 ml) was added dropwise, and the mixture was stirred for 4 h at room temperature. After evaporation of the solvent, the residue was steam distilled to afford a white solid **5** (59 g, 72%). Mp 72–73 °C. IR (KBr): ν 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%.

5-(2-Methylthio-4-methylpyrimidin-5-yl)penta-2,4-diyn-1-ol 6

A mixture of cuprous chloride (1.0 g, 5 mmol), $nC_4H_9NH_2$ (60 ml) and THF–CH_3OH (v/v = 1 : 1, 400 ml) under nitrogen was cooled to 0 °C and hydroxylamine hydrochloride (20 g, 0.288 mol), and compound **5** (41.0 g) were then added in turn. A white precipitate formed, and a solution of 3-bromopropargyl alcohol[8] (0.35 mol) in THF–CH_3OH (v/v = 1 : 1, 100 ml) was then added dropwise. The mixture was stirred again for 5 h at 10–20 °C until the white precipitate disappeared, and was then poured into ice–water (500 ml). The yellow precipitate formed was filtered and recrystallized with 95% ethanol to afford light yellow crystals of **6** (44.1 g, 81%). Mp 127–127.5 °C. IR (KBr): ν 3300 (–OH), 2250 (C≡C), 1560, 1510, 1430 (pyrimidine ring) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 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%.

5-(5-Methacryloyloxypenta-1,3-diynyl)-4-methyl-2-methylthiopyrimidine 7a

1. α-Methylacryloyl chloride. A mixture of α-methylacrylic acid (100 ml) and thionyl chloride ($SOCl_2$, 100 ml) was refluxed for 2 h. A light yellow liquor was distilled at 118 °C/0.1 MPa to afford α-methylacryloyl chloride as a colorless liquid (60 g). IR (KBr): ν 3450, 2930, 2890 (–CH_2–, –CH_3), 1750 (–CO–), 1610 (–C=C–) cm^{-1}.

2. Monomer 7a. A mixture of **6** (2.18 g, 0.01 mol), and α-methylacryloyl chloride (6 ml, 0.082 mol) in dry THF (30 ml) was stirred for 4 h at room temperature and cooled to 0 °C, and a solution of diisopropylamine (6 ml) in dry THF (10 ml) was added dropwise. The mixture was again stirred for 12 h at room temperature and poured into 200 ml ice–water; the precipitate was filtered off and dried. The crude product was recrystallized from *n*-hexane to afford **7a** as a white crystal (2.17 g, 76%). The product turned blue on exposure to visible light. Mp 62 °C. IR (KBr): ν 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}. ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 3H, –C=C–CH_3), 2.54 (s, 3H, pyrimidine –CH_3), 2.55 (s, 3H, pyrimidine –SCH_3), 4.89 (s, 2H, –CH_2–), 5.54 (s, 1H, –C=CH_2), 6.18 (s, 1H, –C=CH_2), 8.46 (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}) (shown in Fig. 6).

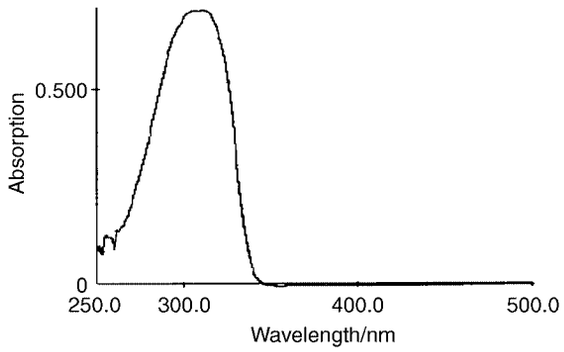


Fig. 6 UV-visible spectrum of **7a** in 1,2-dichloroethane.

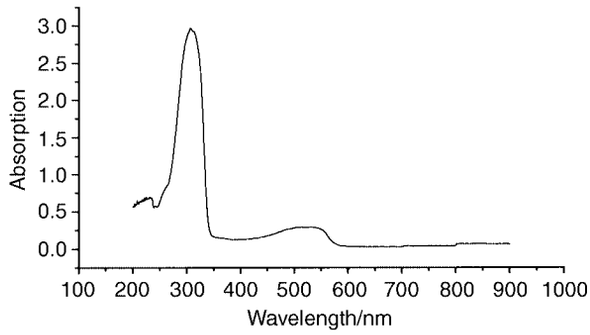


Fig. 7 UV-visible spectrum of polymer **7a** formed by irradiation with a high-pressure mercury lamp (200 W) in chloroform solution.

5-[5-(*p*-Tosyl)oxypenta-1,3-diynyl]-4-methyl-2-methylthiopyrimidine 7b

A mixture of **6** (21.8 g, 0.1 mol) and *p*-tosyl chloride (28.6 g, 0.15 mol) in dry THF (300 ml) was cooled to 0 °C with stirring, and a solution of sodium hydroxide (13.2 g, 0.3 mol) in water (100 ml) was added dropwise. The mixture was stirred again for 7 h at room temperature, filtered, and the filtrate was poured into 500 ml ice–water. The precipitate was filtered off and dried. The crude product was recrystallized from 95% ethyl alcohol to give **7b** as a brown–yellow crystal (30.0 g, 80%). The product turned pink when exposed to daylight. Mp 114–114.5 °C. IR (KBr): ν 2250 (–C≡C–), 1560, 1490, 1350 (pyrimidine ring), 1200, 1150 (–C–O–C–), 950, 765, 710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 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%.

5-(5-Benzenesulfonyloxypenta-1,3-diynyl)-4-methyl-2-methylthiopyrimidine 7c

A solution of **6** (2.2 g, 0.01 mol) and phenylsulfonyl chloride (1.5 ml, 0.012 mol) in dry THF (50 ml) 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 (10 ml) was then added dropwise. The mixture was stirred again for 7 h at room temperature, and poured into 500 ml ice–water, and the yellow precipitate was filtered off and dried. The crude product was recrystallized from 95% ethyl alcohol to give a brown–yellow crystal **7c** (3.2 g, 90%). Mp 89–90 °C. IR (KBr): ν 2900–3050 ($–CH_2–$, $–CH_3$), 2250 (–C≡C–), 1560, 1510, 1430 (pyrimidine ring), 1180 (–C–O–C–), 950, 780, 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H, pyrimidine $–CH_3$), 2.40 (s, 3H, $–SCH_3$), 4.73 (s, 2H, $–CH_2–$), 7.35–7.88 (m, 5H, –Ar), 8.27 (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%.

5-[5-(*m*-Chlorobenzoyloxy)penta-1,3-diynyl]-4-methyl-2-methylthiopyrimidine 7d

A mixture of *m*-chlorobenzoic acid (8 g) and thionyl chloride (100 ml) was refluxed with stirring for 4.5 h to obtain a red-brownish solution, the crude product was used directly for the next reaction. A solution of **6** (1.5 g), and *m*-chlorobenzoyl chloride (1.5 ml) in dry THF (25 ml) was stirred for 8 h at room temperature and white crystals were produced. Stirring was continued for 14 h and the mixture was poured into water (400 ml), and neutralized to pH 7 with sodium hydroxide. A brown–yellow precipitate was produced and filtered, dried, recrystallized with *n*-hexane to afford light yellow crystals of **7d** (1.7 g, 70%). Mp 77–78 °C. IR (KBr): ν 2590 ($–CH_2–$, $–CH_3$), 2250 (–C≡C–), 1720 (–CO–), 1560, 1500, 1410, 1350 (pyrimidine ring) cm^{-1}. ^1H NMR (CCl_4): δ 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%.

5-(5-Propionyloxypenta-1,3-diynyl)-2-methyl-4-methylthiopyrimidine 7e

A solution of **6** (0.8 g), and propionyl chloride (3 ml) in dry THF (35 ml) was stirred for 10 h at room temperature, then cooled to 0 °C. Triethylamine was added dropwise and white crystals were then produced. After stirring again for 5 h, the mixture was poured into water (400 ml) and a yellow precipitate was produced, filtered, dried and recrystallized from ethyl alcohol to obtain yellow crystals of **7e** (0.7 g, 70%). Mp 78–79 °C. IR (KBr): ν 3000–2900 ($–CH_2–$, $–CH_3$), 2250 (–C≡C–), 1740 (–CO–), 1560, 1490, 1410, 1350 (pyrimidine ring) cm^{-1}. ^1H NMR (CCl_4): δ 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%.

Solid-state polymerization

The monomers **7a**, **7b** and **7c** were polymerized by heating the crystals in a vacuum vessel below the melting point or by γ-ray or UV irradiation of the crystals at room temperature. ^{60}Co γ-ray irradiation with a dose rate of 0.1 Mrad h^{-1} or a high-pressure mercury lamp (200 W) without filter was used as the radiation sources for the polymerization; the conversion ratio was determined by extraction of residual monomer with ethanol. The UV-vis spectrum of polymer **7a** (formed by irradiation with a 200 W mercury lamp in chloroform solution) is shown in Fig. 7, $\lambda_{max} = 306.5$ (log $\varepsilon = 4.587$), 533 nm (log $\varepsilon = 3.581$). A comparison of the polymerization rates indicates that ^{60}Co γ-ray irradiation is much more efficient than UV irradiation in inducing polymerization. Time conversion curves for the thermal polymerization of polymers **7b** and **7c** at 95 °C are shown in Fig. 2.

Preparation of polydiacetylene thin films

To a 25 ml three-neck round bottom flask were added diacetylene monomer **7a** (26.60 mg, 0.093 mmol) and NMP (5 mL) under a nitrogen atmosphere. The solution was stirred for 20 min and PMMA (21.05 mg, 0.217 mmol) (**7a**–PMMA = 3 : 7 in mol) was then added at 0 °C. The mixture was stirred at 0 °C for 3 h and then at room temperature for another 48 h under a 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 °C for

48–72 h under a nitrogen atmosphere. The thickness of the blue films was measured on an *alpha-step 250 TENCOR* instrument, and was found to vary from 1.0 to 1.8 μm, depending on the pre-curing time and the spin rate.

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