

## NOTES

## Synthesis and Characterization of Novel Soluble Aromatic Diacetylene- and Thiophene-Containing Polyazomethynes

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Aromatic polyazomethynes have received relatively little attention compared to other polycondensation polymers since the early 60's when a start was made on the development of heat resistant polycondensation polymers. This is generally due to their poor tractability and low hydrolytic stability. Thus, polyazomethynes derived from benzidine,<sup>1</sup> or 1,3,4-oxadiazole- and 1,3,4-thiodiazole<sup>2</sup>-containing diamines are either insoluble totally or soluble in H<sub>2</sub>SO<sub>4</sub> with degradation.

Aromatic polyazomethynes soluble in common organic solvents including chloroform can be prepared from 4,4'-diaminotriphenylmethane and aromatic dialdehydes<sup>3</sup> in *m*-cresole or DMF in the presence of LiCl at room temperature. Soluble aromatic polyazomethynes containing discrete conjugated units may be promising for nonlinear optics application since the polycondensation reaction leads to expansion of the effective conjugation in polymer chain, and the azomethyne links are highly polarizable, which is of importance.

The present authors reported the synthesis, characterization, and nonlinear optical properties of polymers, containing discrete conjugated units of fluorescein<sup>4,5</sup> and arylenevinyldeneethylylydene.<sup>6</sup> The polymers gave films with good optical quality and showed  $\chi^{(3)}$  values up to  $3 \times 10^{-10}$  esu. It is of interest to prepare aromatic soluble polyazomethynes containing discrete conjugated units and study their nonlinear optical properties. This work describes the synthesis and characterization of soluble aromatic polyazomethynes derived from novel conjugated bisaldehydes bearing diphenylbutadiyne- and 2,5-diphenylthiophene groups and 4,4'-diaminotriphenylmethane.

### EXPERIMENTAL

#### Materials

*m*-Cresol was distilled under reduced pressure and other reagent, were used as received (all from Aldrich). 4-Trimethylsilylethynylbenzaldehyde (**1**) and 4,4'-diaminotriphenylmethane (**8**) were prepared according to the literature.<sup>7,8</sup>

#### 2-(4-Trimethylsilylethynylphenyl)-1,3-dioxalane (**2**)

A solution containing compound **1** (16 g, 79 mmol), *p*-toluenesulfonic acid (0.1 g), ethyleneglycol (5.9 g, 95 mmol), and benzene (350 ml) was slowly distilled until carbonyl absorption disappeared completely from the IR spectra (4 h). The reaction mixture was washed with

dilute K<sub>2</sub>CO<sub>3</sub> solution and chromatographed on SiO<sub>2</sub> (benzene). Yield = 88%, mp = 40–42°C. IR (cm<sup>-1</sup>) 2145 (C≡CSi(CH<sub>3</sub>)<sub>3</sub>), <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) 7.42 (d, 2H, *J* = 8.4 Hz, *meta* to C≡C), 7.38 (d, 2H, *J* = 8.4 Hz, *ortho* to C≡C), 5.79 (s, 1H, CH aliph), 4.10–3.95 (m, 4H (CH<sub>2</sub>)<sub>2</sub>), 0.21 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) 138.1 (>CH–C<sub>ar</sub>), 132.1, 126.5 (CH<sub>ar</sub>), 104.9 (–C≡C–Si), 103.7 (CH aliph), 94.5 (–C≡C–Si), 65.7 (CH<sub>2</sub>), 0.0 (CH<sub>3</sub>).

#### 2-(4-Ethynylphenyl)-1,3-dioxalane (**3**)

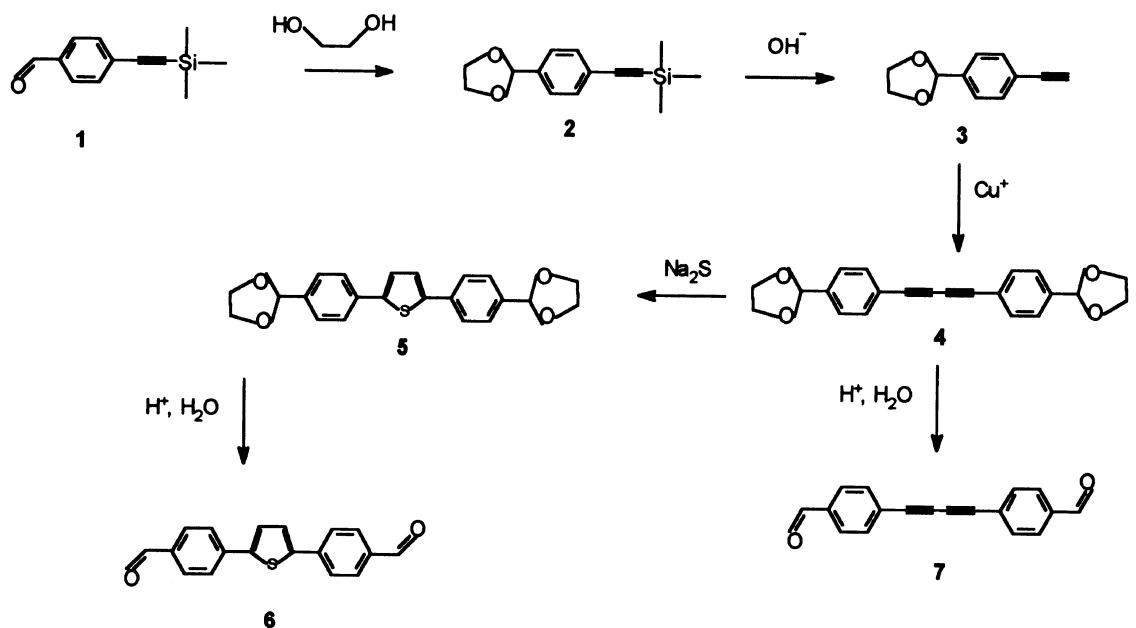
A solution of compound **2** (24.7 g, 100 mmol) and KOH (1 g) in methanol (250 ml) was stirred for 2 h at room temperature. The reaction mixture was poured into water and the precipitate formed was filtered off washed with water and dried *in vacuo*. Yield 80%, mp = 44–46°C. IR (cm<sup>-1</sup>) 3320 (≡CH), 2100 (C≡CH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm), 7.42 (d, 2H, *J* = 8.4 Hz, *meta* to C≡C), 7.32 (d, 2H, *J* = 8.4 Hz, *ortho* to C≡C), 5.67 (s, 1H, CH aliph), 4.00–3.85 (m, 4H (CH<sub>2</sub>)<sub>2</sub>), 2.99 (s, 1H, ≡CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) 138.5 (>CH–C<sub>ar</sub>), 132.2, 126.4 (CH<sub>ar</sub>), 103.7 (CH aliph), 83.8 (–C≡CH), 78.0 (–C≡CH), 65.7 (CH<sub>2</sub>).

#### Diphenylbutadiyne-4,4'-bis-[2-(1,3-dioxalane)] (**4**)

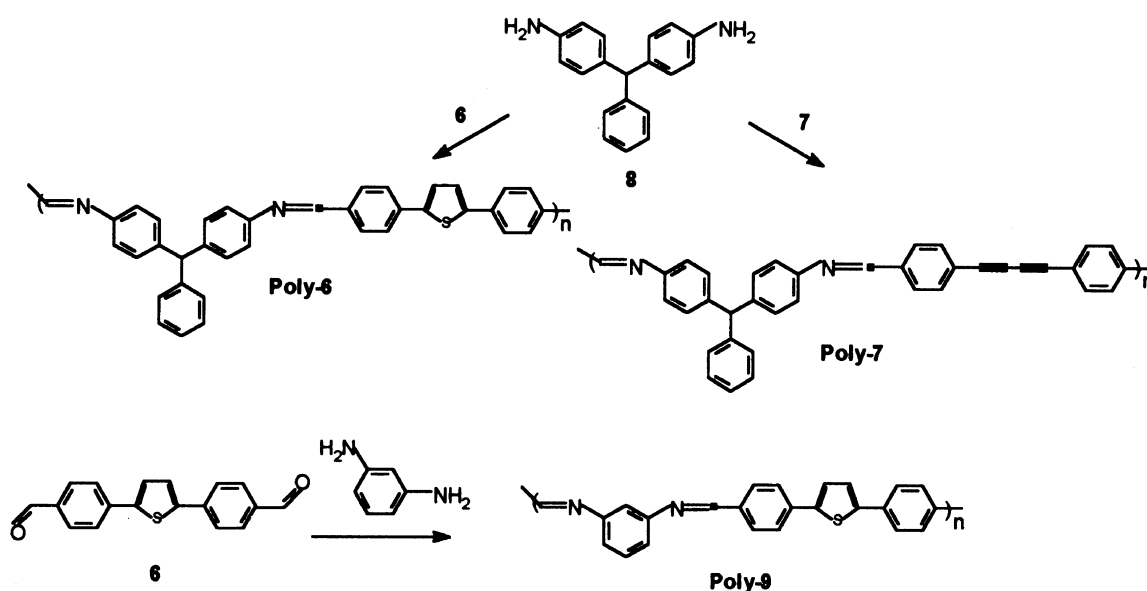
Oxygen was bubble through a solution containing compound **3** (2 g, 11.4 mmol), CuCl (0.05 g), *N,N,N',N'*-tetramethylenediamine (0.5 ml) in 2-propanol (10 ml) for 3 h. The reaction mixture was poured into diluted ammonia solution, and the precipitate was collected, washed with water and crystallized from *n*-butanol. Yield 50%, mp = 180–181°C. IR (cm<sup>-1</sup>) 2145 (C≡C–C≡C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm), 7.43 (d, 4H, *J* = 8.4 Hz, *meta* to C≡C), 7.34 (d, 4H, *J* = 8.4 Hz, *ortho* to C≡C), 5.68 (s, 2H, CH aliph), 4.00–3.85 (m, 8H (CH<sub>2</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) 138.3 (>CH–C<sub>ar</sub>), 132.1, 126.7 (CH<sub>ar</sub>), 103.7 (CH aliph), 82.5 (Ph–C≡), 76.2 (≡C–C≡), 65.5 (CH<sub>2</sub>).

#### 2,5-Diphenylthiophene-4,4'-bis-[2-(1,3-dioxalane)] (**5**)

To a solution of compound **4** (6.6 g, 19.2 mmol) in dioxane (200 ml) NaS × H<sub>2</sub>O containing 35% of Na<sub>2</sub>S (5.35 g, 24 mmol) dissolved in water (20 ml) was added at room temperature with stirring. The solution pH was brought to 8–9 by adding concentrated hydrochloric acid and stirred for 48 h. The conversion was monitored by IR using diacetylene stretching at 2145 cm<sup>-1</sup>. After the disappearance of diacetylene stretching, the reaction



Scheme 1. Monomer synthesis.



Scheme 2. Polymer synthesis.

mixture was poured in water, the precipitate was filtered off washed with water and crystallized from a mixture benzene-ethanol. Yield 50%, mp = 180–182°C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm), 7.61 (d, 4H,  $J=8.4$  Hz, *ortho* to  $\text{CH} < \text{O}_2$ ), 7.47 (d, 4H,  $J=8.4$  Hz, *meta* to  $\text{CH} < \text{O}_2$ ), 7.27 (s, 2H,  $\text{H}^3$  of thiophene) 5.81 (s, 2H, CH aliph), 4.00–3.85 (m, 8H  $(\text{CH}_2)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm) 143.9 ( $\text{C}_{\text{ar}}-\text{S}$ ), 137.5 ( $>\text{CH}-\text{C}_{\text{ar}}$ ), 135.5 ( $\text{C}_{\text{ar}}$  *para* to  $\text{O}_2 > \text{CH}$ ), 126.9 ( $\text{C}_{\text{ar}}$  *ortho* to  $\text{O}_2 > \text{CH}$ ) 125.9 ( $\text{C}_{\text{ar}}$  *meta* to  $\text{O}_2 > \text{CH}$ ), 124.3 (CH of thiophene), 103.5 ( $\text{O}_2 > \text{CH}$ ), 65.8 ( $(\text{CH}_2)_2$ ).

#### 2,5-Diphenylthiophene-4',4''-dialdehyde (6)

Compound 5 (3.1 g, 8.2 mmol) was dissolved in acetic acid (150 ml) and three drops of concentrated HCl dissolved in water (5 ml) were added to the solution. The reaction mixture was stirred 24 h at 50°C. The precipitate formed was filtered off, dried and chromatographed

on  $\text{SiO}_2$  in benzene. Yield 81%, mp = 148–150°C, IR ( $\text{cm}^{-1}$ ) 1700 (C=O, aldehyde).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm), 10.0 (s, 2H, CH=O), 7.91 (d, 4H,  $J=9.2$  Hz, *ortho* to CH=O), 7.83 (d, 4H,  $J=9.2$  Hz, *meta* to CH=O), 7.51 (s, 2H,  $\text{H}^3$  of thiophene).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm) 191.5 (CH=O), 143.9 ( $\text{C}_{\text{ar}}-\text{S}$ ), 139.2, 135.8 ( $\text{O}=\text{CH}-\text{C}_{\text{ar}}$ ,  $\text{C}_{\text{ar}}$  *para* to O=CH), 130.4 ( $\text{C}_{\text{ar}}$  *ortho* to O=CH), 126.1 (CH of thiophene), 125.9 ( $\text{C}_{\text{ar}}$  *meta* to O=CH).

#### Diphenylbutadiyne-4,4'-dialdehyde (7)

To a solution of compound 4 (3.5 g, 10.2 mmol) dissolved in dioxane (180 ml) three drops of concentrated HCl in water (5 ml) were added at 60°C. The reaction mixture was stirred for 5 h at 60°C and cooled. The precipitate formed was filtered off washed with water and dried. Yield 90%,  $T_m=248$  (dec). IR ( $\text{cm}^{-1}$ ) 2210, 2145 ( $\text{C}\equiv\text{CC}\equiv\text{C}$ ), 1693 (C=O, aldehyde).

### Polymerization

**Method 1.** To a solution of diamine **8** or *m*-phenylenediamine (1.8 mmol) in *m*-cresole (5 ml) an equivalent amount of solid dialdehyde **6** or **7** was added under nitrogen. The reaction was stirred at room temperature until the ratio of CH=O ( $1700\text{ cm}^{-1}$ ) to CH=N-stretching ( $1620\text{ cm}^{-1}$ ) in the IR spectra became constant. Polymer solution was precipitated in methanol, and the precipitate was washed with methanol and dried *in vacuo* at  $60^\circ\text{C}$ .

**Method 2.** To a solution of diamine **8** (1.8 mmol) in *m*-cresole (5 ml) an equivalent amount of solid dialdehyde **6** or **7** was added. The reaction vessel was evacuated to 1 mmHg and the reaction was carried out at  $40\text{--}50^\circ\text{C}$  with stirring until the ratio of CH=O ( $1700\text{ cm}^{-1}$ ) to CH=N-stretching ( $1620\text{ cm}^{-1}$ ) in the IR spectra was constant. The polymer solution was precipitated in methanol, and the precipitate was washed with methanol and dried *in vacuo* at  $60^\circ\text{C}$ .

### Measurements and Sample Preparation

The number average molecular weight ( $M_n$ ) of polymers Poly-6 and Poly-7 were determined by  $^1\text{H}$  NMR spectroscopy using signals of azomethyne (8.45 ppm) and terminal formyl protons (10.0 ppm).  $M_n$  of insoluble Poly-9 was estimated from IR spectra using C=O stretching at  $1700\text{ cm}^{-1}$  of terminal aldehyde group and azomethyne stretching at  $1620\text{ cm}^{-1}$  and IR and  $^1\text{H}$  NMR data of soluble polymers Poly-6 and Poly-7. DSC and TGA were performed at a heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen with a du Pont 2100 machine. FT-IR-spectra were taken using a Nicolet 510p spectrometer for films cast from chloroform. UV-visible spectra were taken using a Shimadzu UV-260 spectrometer in chloroform solution.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were taken using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in  $\text{CDCl}_3$  with TMS as an internal standard. All  $\chi^{(3)}$  data were obtained using the picosecond laser consisting of a mode locked Quantel Nd:YAG laser with frequency doubled to 532 nm.

## RESULTS AND DISCUSSION

Monomers **6** and **7** were prepared by the deprotection of bisacetals **5** and **4**, respectively. The protection of aldehyde function by the acetal formation makes aldehyde insensitive to nucleophilic attack avoiding undesirable side reactions when removed trimethylsilyl group and nucleophilic addition of  $\text{H}_2\text{S}$  to the diacetylene moiety. The bisacetal **5** was synthesized from bisacetal **4** by the addition of  $\text{H}_2\text{S}$  to diacetylene under basic conditions to produce thiophene derivative **5**. Bisacetal **4** was, then, dimerized by the oxidative coupling reaction of acetylene-terminated acetal **3**. Acetal **3** was prepared starting from trimethylsilylethynyl benzaldehyde (**1**) by the protection of aldehyde to give 2-(4-trimethylsilylethynylphenyl)-1,3-dioxalane (**2**) followed by deprotection of the acetylene moiety.

Polymers Poly-6, Poly-7, and Poly-9 were prepared by polycondensation in *m*-cresol. Two different ways were used to carry out the polycondensation. In the first case, the reagents (diamine and dialdehyde) were allowed to react at room temperature under nitrogen flow (Method

I). Poly-6 and Poly-7 prepared in this way were soluble in chloroform and gave transparent brittle films when cast from solution. Poly-9 was insoluble in common organic solvents and precipitated from the reaction mixture during polycondensation. In the second case, polycondensation was carried out at  $40\text{--}50^\circ\text{C}$  under the reduced pressure (1 mmHg) to remove water formed during the reaction (Method II). This method was applied only for the preparation of Poly-6 and Poly-7.

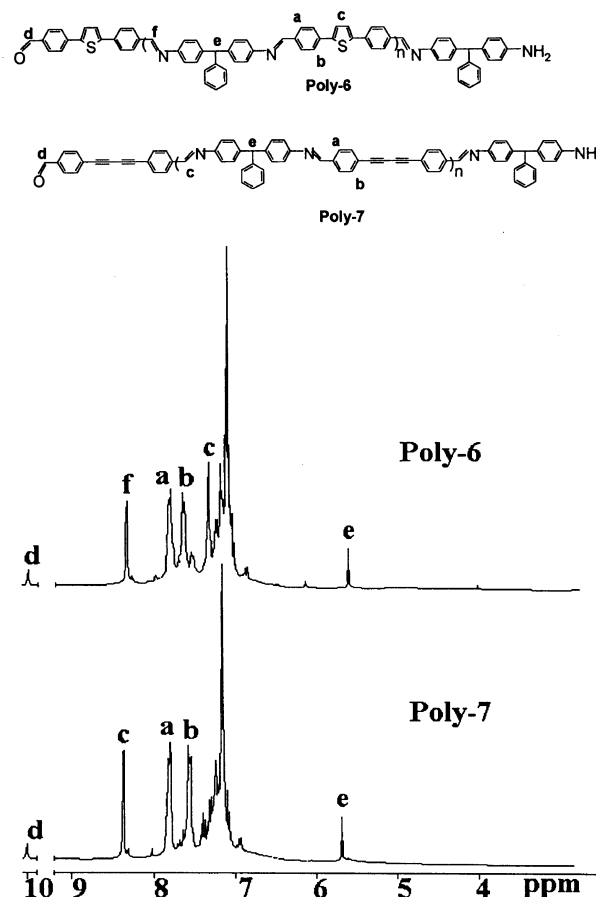


Figure 1.  $^1\text{H}$  NMR spectra of Poly-6 and Poly-7 prepared by method 2.

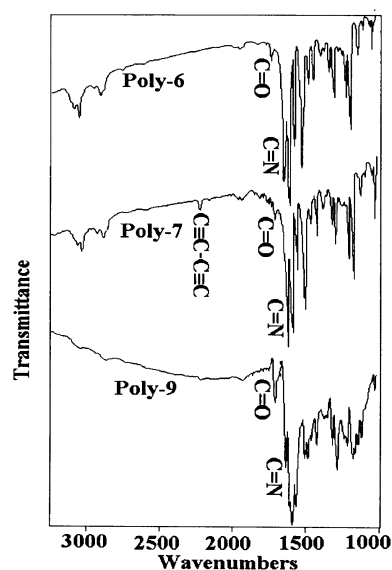


Figure 2. FT-IR spectra of Poly-6, Poly-7 (prepared by method 2), and Poly-9.

Table I. Polymerization results

Polymer	Method	Polymer yield/%	$M_n$	$\lambda_{\max}$	DP	$T_g$	Solubility in chloroform
				nm		°C	
Poly-6	I	83	1050	368	4	130	+
Poly-7	I	85	1470	386	6	—	+
Poly-9	I	77	730	—	4	150	—
Poly-6	II	91	3160	370	12	128	+
Poly-7	II	90	3000	387	11	—	+

The polymer structures were determined by the usual spectroscopic techniques. Figures 1 and 2 present  $^1\text{H}$  NMR and IR spectra of polymers. As can be seen from the figures, the assignment of the signals corresponds to the proposed polymer structure. The results of polymerization are summarized in Table I. As can be seen from the table when removing water from the reaction mixture the molecular weight of polymers increased.

In spite of the rather low molecular weight of polymers, all even those prepared by method I with DP of 4–6 gave films with good optical quality when cast onto a quartz plate from chloroform solution. The polymers were highly amorphous according to X-ray diffraction, probably, due to the bulky triphenylmethyl group. TGA showed Poly-6, Poly-7, and Poly-9 to exhibit good thermostability with 10% weight loss at 490, 510, and 490°C, respectively. Neither Poly-6 nor Poly-9 showed any peak on the DSC curves. Poly-7 showed an exotherm at 260°C due to the thermal cross-linking of polymer by diacetylene groups since the sample lost solubility after DSC run and diacetylene stretching disappeared from the IR spectra. Probably, the thermal cross-linking of Poly-7 is the reason for the somewhat higher thermostability of this polymer compared to others. No glass transition was detected in the DSC curves of Poly-7 probably due to the thermal cross-linking starting at about 180°C. Poly-7 did not undergo topochemical polymerization by diacetylene groups on heating or irradiation due to its amorphous nature. Wei *et al.* reported the synthesis and thermal properties of some insoluble diacetylene-containing aromatic polyazomethynes prepared by the oxidative polymerization of acetylene-terminated Schiff bases.<sup>9</sup> These polymers showed exotherms in the DSC traces peaking at around 200°C related to the cross-linking by diacetylene moiety and exhibited 10% weight loss at 510°C, similarly to Poly-7.

Figure 3 shows UV-absorption spectra of chloroform solutions of Poly-6, Poly-7, and monomer **6**. Poly-6 presents a red shift of the long wave absorption maximum (387 nm) of about 25 nm compared to that of monomer **6** which is, probably due to a slight expanding of the conjugated system in the polymer. Poly-7 shows a long wave absorption maximum at 370 nm. This blue shift compared to Poly-6 may be related to the poorer conjugation between double and triple bonds than between double bonds.

Preliminary  $\chi^{(3)}$  of polymer films were of the order of  $10^{-11}$  esu. This represents an intrinsic non-resonance enhanced value since the polymers showed no absorption at 532 nm (the wavelength used for the measurements). Thus, well-known third-order non-linear materials as polyconjugated polymers exhibit  $\chi^{(3)}$  from  $10^{-12}$  to  $10^{-9}$

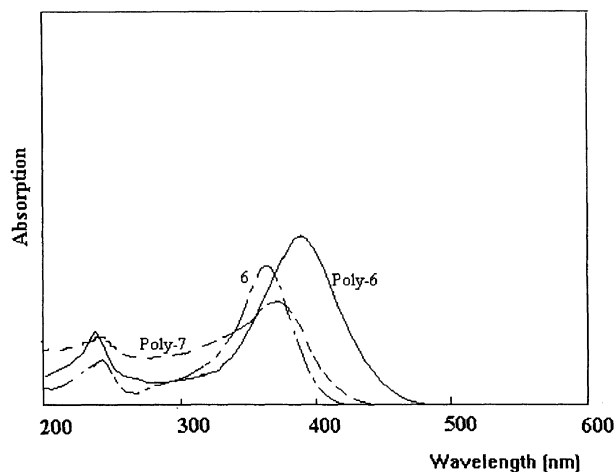


Figure 3. UV-absorption spectra of chloroform solutions of monomer **6** and Poly-6 and Poly-7 prepared by method 2.

esu (polydiacetylenes)<sup>10</sup> and sometime to  $10^{-8}$  esu (polyacetylene).<sup>10</sup> However, these materials are not easy to process into thin transparent films, and they sometimes are not stable in air. Taking into account the excellent optical quality of the films, and rather high  $\chi^{(3)}$  these polymers should prove applicable to non-linear optics.

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