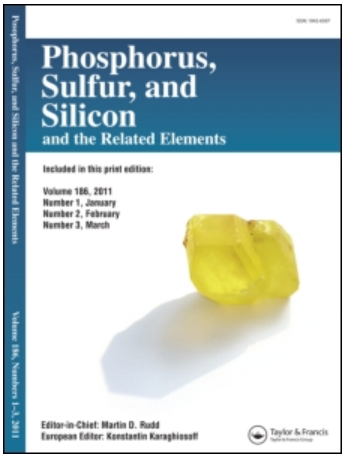

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SYNTHESIS, SOME SPECTROSCOPIC AND ELECTROCHEMICAL INVESTIGATIONS ON NOVEL MONOMERIC AND POLYMERIC ACETYLENE SUBSTITUTED THIOPHENE MONOMERS AND POLYMERS

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SYNTHESIS, SOME SPECTROSCOPIC AND ELECTROCHEMICAL INVESTIGATIONS ON NOVEL MONOMERIC AND POLYMERIC ACETYLENE SUBSTITUTED THIOPHENE MONOMERS AND POLYMERS

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Acetylene substituted thiophenes of the following types were synthesized:

Ar-≡-Ar-≡-Ar, Ar'-≡-Ar-≡Ar', Ar-≡-Ar'-≡-Ar, Ar'-≡-Ar-Ar-≡-Ar',

Ar-≡-Ar- Ar'-≡-Ar'; Ar' = Ar = 

These monomers were polymerized to the corresponding polymers. The UV-spectra and their oxidation potentials were determined. Attempts to correlate these two properties will be reported. The corresponding polymers were of relative low molecular weight and are non-conductors in the doped as well as iodine doped state.

Keywords: Acetylene substituted thiophenes; polymeric acetylene substituted thiophenes; oxidation potentials; UV-spectra

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[†]Ph.D. Thesis, Univ. of Cincinnati, 1991.

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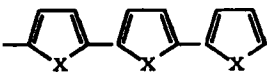


INTRODUCTION

Poly(acetylenes) have been shown to have a high conductivity on charge-transfer doping.[1] Poly(heteroarylenes) which have a structural similarity with poly(acetylene) by assuming that the CH-units are formed by the heteroatoms into an acetylenic type polymer. Therefore, it was not surprising when it was found that such polymers derived of pyrrole[2], thiophene[3,4] and others showed a remarkable conductivity.[5] We became interested in the synthesis, UV-spectroscopic and electrochemical properties of poly(thiophenes) when we succeeded to polymerize 3-methyl-2,5-dibromothiophene utilizing n-butyl lithium and copper(II)chloride[6] and subsequently investigated in a series of papers the synthesis of oligo-2,5-bithienyls and the correlation of their UV-spectra with their oxidation potentials.[7–13] The synthesis and polymerization of oligomeric dialkylthiophenes[14] and of functionalized poly(thiophenes) was reported recently[5] as was the synthesis of a number of oligothiophenes with potent biological activity.[15]

Vinyl substituted thiophenes, their polymerization and some electrochemical properties were reported by Kossmehl and co-workers.[16] Some acetylene substituted thiophenes and electrochemical properties of polymers derived of these species were described for the first time by a Japanese group.[17]

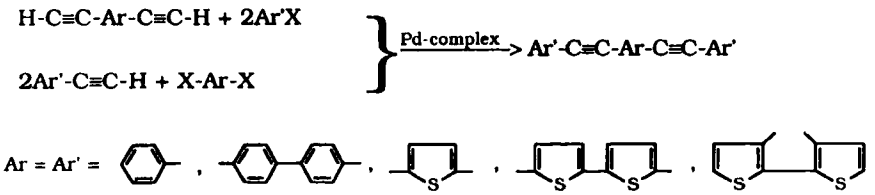
In the following study, as a continuation of our attempts to correlate UV-spectra and oxidation potentials of thiophenes containing monomers in dependency of steric hindrance, we report on the synthesis of a series of novel phenyl and thiophene substituted acetylenes and discuss their UV-spectra and their oxidation potentials. In addition, we also describe the polymerization and conductivity of these novel thiophenes.

RESULTS AND DISCUSSION

I. Synthesis and Characterization of the Monomers

In our earlier papers on this subject we found that UV-spectra and oxidation potentials of oligothiophenes correlated well with steric hindrance. That is, if due to substituents the thiophene species are impeded from assuming coplanarity, the λ_{max} of the UV-spectra show a bathochromic shift while their oxidation potentials increase to more positive values. To further check these correlations as

well as an attempt to obtain useful conducting materials, the following novel thiophene derivatives were prepared. Their synthesis proceeded according to Scheme I.



SCHEME I

The palladium complex used was the one introduced by Yamamoto and coworkers,[17] namely tetrakis(triphenylphosphine) palladium(O). In Table I the according to Scheme I obtained monomers are listed. The monomers M1–M9 were prepared using the Pd-catalyzed C-C coupling reaction to effect the condensation of two monoacetylene substituted aromatic compounds with dihaloaromatic compounds and diacetylene substituted aromatic compounds with monohaloaromatics, as well as triacetylene substituted aromatic compounds with monohalo aromatics. In Tables II, III, and IV the conditions and results of each of the coupling reactions are listed. The elemental analyses, melting points, and ^{1}H-NMR-spectra of the monomers M1–M9 are collected in Table V.

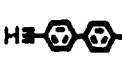
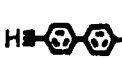
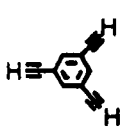
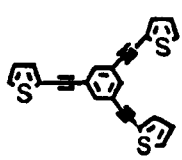
The IR-spectra of M1–M9 are also in agreement with the assigned structures.

II. Electrochemical, UV and Visible Spectra Studies of the Monomers

Oxidation potentials for the monomers of interest were determined via cyclic voltammetry techniques. A single compartment cell with the classic three electrode configuration (working electrode and standard calomel electrode) was used. The electrolytic medium consisted of the monomer dissolved in methylene chloride with tetrabutylammonium tetrafluoroborate as supporting electrolyte (10^{-1} M) as previously described by us.[9].

As we have shown earlier the λ_{max} and ε_{max} values of simple thiophene oligomers increase as expected while the oxidation potentials decreases (also as expected) in dependency of the number of thiophene units of the oligomers. Extending the length of the conjugated system and, thus, gaining an increase in delocalization for the derived radical cations manifests itself by decreasing values for the oxidation potentials. These peak potentials represent an irreversible oxidation and the reaction is probably a 2-electron process[12] (Table VI).

TABLE I Preparation of the Monomers

Acetylene	Dibromo	Products	
			M1
			M2
			M3
			M4
Diacetylene	**Monobromo**	**Products**	
			M5
			M6
			M7
			M8
Triacetylene	**Monobromo**	**Product**	
			M9

The UV and visible spectra of the novel monomers fall in the λ_{max} range of 305–384.7 nm (Table VII). Molar absorptivity values, ε (M^{-1} cm^{-1}), were calculated from the slope obtained by plotting absorbance vs. concentration.

TABLE II Pd-catalyzed coupling reactions between X-Ar-X and Ar-C≡CH

No	*X-Ar-X*	*Ar-C≡CH*	*Catalyst*	*Base*	*Temp °C*	*Time h*	*Yield %*	*Product Color*
M1	$C_4H_2SBr_2$	C_6H_4S	$Pd(PPh_3)_4$ +CuI	NEt_3	95	12	60	Yellow
M2	$C_4H_2SBr_2$	C_8H_6	$Pd(PPh_3)_4$ +CuI	NEt_3	95	12	75	Pale Yellow
M3	$C_8H_4S_2Br_2$	C_8H_6	$Pd(PPh_3)_4$ +CuI	NEt_3	95	24	75	Yellow
M4	$C_{10}H_8S_2Br_2$	C_8H_6	$Pd(PPh_3)_4$ +CuI	NEt_3	95	24	60	Yellow

High values for λ_{max} and ε_{max} indicate a long conjugated system to be present in the monomeric molecules.

If one inspects now the λ_{max} values for some of the novel acetylenic compounds it becomes evident from these values for M1 to M8 that no such clear-cut relationship exists for these acetylenic compounds. Thus, comparing for example M2 with M5, both compounds have identical chromophores, except that in M5 the thienyl moieties are at the end, whereas in M2 the compound is end capped by the phenyl groups with the latter species exhibiting a slightly larger wave length position than the first one. The difference between the λ_{max} positions amounts to 9 nm. If one inspects the λ_{max} values of M7 with the one of M3 one finds, in spite of the fact that both compounds again have identical chromophores except for the positions of the thienyl and phenyl groups, that there is a considerable difference in the corresponding λ_{max} values, namely 47.3 nm. Also for this case a satisfactory explanation cannot be given at present, unless one argues that the favored conformation of the thiophene ring in M3 is 5-trans. However, then one excludes the possibility that there is a certain amount of steric hindrance between the hydrogen atoms of the 3- and 3′-positions and the unshared pairs of electrons of the ring sulfur atoms.[12] Also, steric factors hardly can be invoked to explain the difference in the positions of the λ_{max} of M4 and M8. We are presently undertaking molecular modeling to get more insight in this problem. Similar observations are made if one compares compounds in which the aryl moieties are separated by vinyl groups with their analogs in which the identical aryl groups are present but are separated by an acetylenic group. From the positions of the λ_{max} values the conclusion can be

TABLE III Pd-catalyzed coupling reactions between Ar-X and Ar-$(C{\equiv}CH)_2$

No	*Ar-X*	*Ar-$(C{\equiv}CH)_2$*	*Catalyst*	*Base*	*Temp °C*	*Time h*	*Yield %*	*Product Color*
M5	C_4H_3SBr	p-$C_{10}H_6$	$Pd(PPh_3)_4$ +CuI	NEt_3	95	12	75	Pale-Yellow
M6	C_4H_3SBr	m-$C_{10}H_6$	$Pd(PPh_3)_4$ +CuI	NEt_3	95	12	80	White
M7	C_4H_3SBr	$C_{16}H_{10}$	$Pd(PPh_3)_4$ +CuI	NEt_3	95	24	60	Yellow
M8	C_5H_5SBr	$C_{16}H_{10}$	$Pd(PPh_3)_4$ +CuI	NEt_3	95	24	70	Yellow

TABLE IV Pd-catalyzed coupling reactions between Ar-X and Ar-(C≡CH)$_3$

No	*Ar-X*	*Ar-(C≡CH)$_3$*	*Catalyst*	*Base*	*Temp °C*	*Time h*	*Yield %*	*Product Color*
M9	C_4H_3SBr	$C_{10}H_6$	$Pd(PPh_3)_4$ +CuI	NEt_3	95	36	40	Yellow

TABLE V ^{1}H NMR, m.p. and elemental analyses of M1-M9

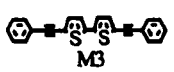
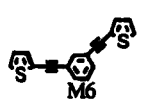
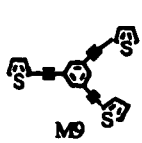
Structure formula	*m.p. C*	*HNMR (ppm) CDCl*	*Elemental analyses (calc/found) % C*	*H*
 M1	117-118	7.29-7.33 (m, 4H) 7.14 (s,2H) 7.00-7.03(m, 2H)	64.83 65.05	2.72 2.96
 M2	86-87	7.503-7.524 (m, 4H) 7.335-7.340 (m, 6H) 7.15 (s,2H)	84.47 84.60	4.25 4.50
 M3	165-166	7.47-7.57 (m,4H) 7.30-7.40 (m,6H) 7.17 (d, j=3.82 Hz, 2H) 7.07 (d, j=3.82 Hz, 2H))	78.65 78.70	3.85 4.00
 M4	114-115	7.48-7.53 (m,4H) 7.31-7.36 (m,6H) 7.10 (s, 2H) 2.20 (s, 6H)	79.19 78.96	4.57 4.57
 M5	204-205	7.49 (s, 4H) 7.29-7.33 (m, 4H) 7.01-7.04 (m, 2H)	74.45 74.35	3.47 3.59
 M6	162-163	7.67-7.68 (m, 1H) (7.45-7.49 (m, 2H) 7.28-7.36 (m, 5H) 7.00-7.03 (m, 2H)	74.45 74.25	3.47 3.62
 M7	decomposed above 220°C	7.59 (s, 8H) 7.315 (dd, 4H) 7.025 (t, 2H)	78.65 78.42	3.85 4.00
 M8		7.60 (s, 8H) 7.20(d, J=5 Hz, 2H) 6.885 (d, J=5Hz, 2H) 2.42 (s, 6H)	79.19 79.32	4.57 4.70
 M9	decomposed above 230°C	7.61 (s, 3H) 7.21-7.33 (m,6H) 7.025(t, 3H)	72.69 72.73	3.05 3.18

TABLE VI λ_{max}, ε_{max} and E^{ox} values of thiophene oligomers

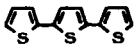
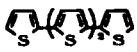
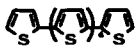
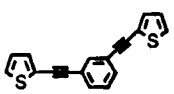
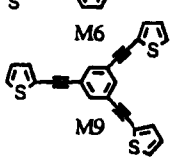
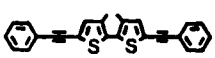
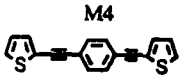
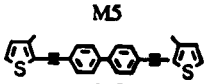
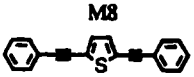
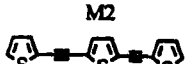
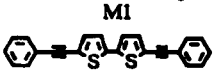
	UV (l_{max}, $CHCl_3$)	*ε (M^{-1} cm^{-1})*	*E_{ox} (VOLT)*
	302	12470	1.28
	355	25050	1.05
	390	45500	0.97
	432	60000	0.46

TABLE VII λ_{max}, ε_{max} and E^{ox} values of M1–M9

Structural Formula	*UV (λ_{max}, $CHCl_3$)*	*ε ($M^{-1}.cm^{-1}$)*	*E^{0}_{ox} (VOLT)*
 M6	305.6	49,975	1.51
 M9	309.6	47,861	N.R.
 M7	337.4	30,129	2.28
 M4	337.8	33,779	1.22
 M5	339.8	76,229	1.415
 M8	344.4	105,146	1.46
 M2	348.8	33,075	1.5
 M1	366.6	39,345	1.3
 M3	384.7	44,311	N.R.

drawn that delocalization of electrons through the chromophore of the vinyl group containing compounds is more effective than in the corresponding acetylenes. This statement is confirmed by the much lower oxidation potentials of the vinyl analogs, which indicate that the corresponding radical cations are more stable than the ones derived of the acetylene analogs (Table VIII).

PREPARATION AND ELECTROCHEMISTRY OF THE POLYMERS

The polymerization of M1–M8 was accomplished with a Pd-complex promoted catalysis. The repeating units of the polymers made in this fashion are shown in Table IX.

In Table X conditions and yields of P1–P8 are listed. The polymers P1–P8 have a low solubility in common organic solvents. Differential scanning calorimetry (DSC) thermograms of these polymers indicate a high degree of thermal stability. No degradation occurs between 40°C to 340°C. Glass transition temperatures (T_g) or melting temperatures (T_m) were not observed in this region. Low solubility prevented the measuring of molecular weights by conventional methods. However, by making the assumption that a bromide is located at both ends of the oligomers, the approximate molecular weights of the oligomers were calculated from their bromine contents. Molecular weights of P1–P8 were found to be in the range of 1300–2100 daltons (Table XI). This indicates that there are very few repeating units in each molecule (approximately 4–7).%

TABLE VIII Comparison of λ_{max} and E°_{ox} -Values of Selected acetylenes and Their Vinyl Analogs

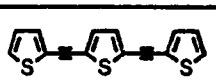
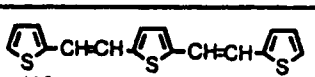
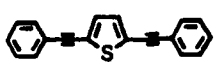
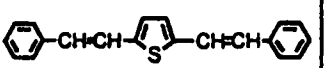
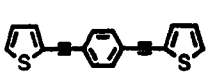
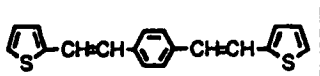
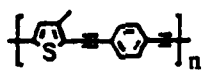
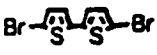
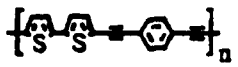
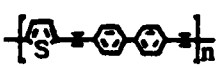
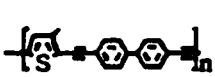
$\lambda_{max}(CHCl_3)$	E°_{OX}	$\lambda_{max}(CHCl_3)$	E°_{OX}
			
366.6	1.3	413	0.95
			
348.8	1.5	391	1.10
			
339.8	1.415	377	0.83

TABLE IX Preparation of Polymers

Diacetylene	Dibromo	Polymers
		 P1
		 P2
		 P3
		 P4
		 P5
		 P6
		 P7
		 P8

All these polymers contain a toluene soluble fraction which is designated to the low molecular weight polymer. The insoluble fraction then represents the high molecular fraction.

The percentage of low and high M.W. polymers by these methods is shown. The relative high percentage of the low M.W. determines that the low solubility of high M.W. polymers in the polymerization solvent seems to prevent further chain growth (Table XII).

The polymers P1–P-8 are insulators. Only a moderate increase in conductivity was observed after the polymers were doped with iodine. Doping was accomplished by exposing the polymers to iodine vapor for 24 hours. Conductivities for the polymers before and after doping, are listed in Table XIII.

TABLE X Pd-Catalyzed Polycondensation between X-Ar-X and Ar-$(C{\equiv}CH)_2$

Run	*X-Ar-X*	*Ar-$(C{\equiv}CH)_2$*	*Catalyst*	*Temp °C*	*Time h*	*Yield %*	*Products*
1	$C_4H_2SBr_2$	$C_{10}H_6$	$Pd(PPh_3)_4$ +CuI	95	2	91.3	P1
2	$C_5H_4SBr_2$	$C_{10}H_6$	$Pd(PPh_3)_4$ +CuI	95	2	97.9	P2
3	$C_8H_4S_2Br_2$	$C_{10}H_6$	$Pd(PPh_3)_4$ +CuI	95	2	96.4	P3
4	$C_{10}H_8S_2Br_2$	$C_{10}H_6$	$Pd(PPh_3)_4$ +CuI	95	2	93.2	P4
5	$C_4H_2SBr_2$	$C_{16}H_{10}$	$Pd(PPh_3)_4$ +CuI	95	2	73.7	P5
6	$C_5H_4SBr_2$	$C_{16}H_{10}$	$Pd(PPh_3)_4$ +CuI	95	2	77.1	P6
7	$C_8H_4S_2Br_2$	$C_{16}H_{10}$	$Pd(PPh_3)_4$ +CuI	95	2	90.9	P7
8	$C_{10}H_8S_2Br_2$	$C_{16}H_{10}$	$Pd(PPh_3)_4$ +CuI	95	2	97.1	P8

IR spectra of P1–P8 are consistent with the assigned structures. They show the γ (C≡C) band at about 2200 cm^{-1}, the δ (C-H) band of the phenylene unit at 820–835 cm^{-1} and δ (C-H) of thiophene unit at 800–810 cm^{-1}. The γ (C-H) band of terminal -C≡CH group near 3300 cm^{-1} does not show up in their IR spectra, supporting the assumption that bromine atoms are at the ends of the polymeric chain.

TABLE XI Elemental Analyses, Color and Approximate Molecular Weight for P1–P8

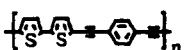
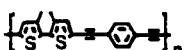
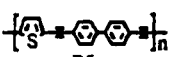
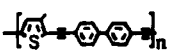
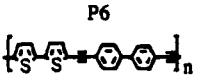
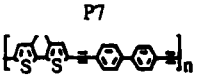
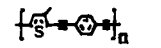
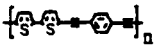
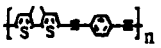
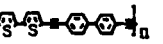
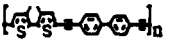
Polymers	*M.W.*	*Color*	*Elemental analyses*		
			%C (found)	*%H (found)*	*%Br (found)*
 P1	1470	yellow-green	77.64	3.74	7.85
 P2	1597	yellow-brown	76.89	3.73	7.39
 P3	1397	brown	69.54	3.04	9.55
 P4	1824	green-brown	71.47	3.76	7.31
 P5	2109	green	74.01	3.83	5.70
 P6	1940	green	77.43	4.00	6.38
 P7	1612	green	74.03	3.60	8.46
 P8	1760	yellow-green	72.00	3.98	7.85

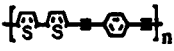
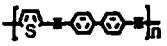
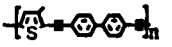
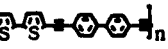
TABLE XII Percentage of Low M. W., High M. W. and Total Yield of P1–P8

Polymers		*% Low M. W.*	*% High M. W.*	*Total % Yield*
	P1	43.5	47.8	91.3
	P2	42.6	55.3	97.9
	P3	26.8	69.6	96.4
	P4	33.9	59.3	93.2
	P5	43.6	29.1	73.7
	P6	33.3	43.8	77.1
	P7	42.4	48.5	90.9
	P8	40.6	56.5	97.1

EXPERIMENTAL

Toluene was used as the polymerization solvent. It was purified and dried in the usual manner.[18] Tetrakis(triphenylphosphine) palladium(O), $Pd(PPh_3)_4$, was prepared according to the literature.[19] Copper(I) iodide, CuI, NEt_3, 2-bromothiophene, 2,5-dibromothiophene, 1,4-dibromobenzene and pheny-

TABLE XIII Electrical Conductivities of P1–P8

Polymers		*Conductivity* $ohm^{-1} \times cm^{-1}$	*% I_2*	*Conductivity After I_2doping* $Ohm^{-1} \times cm^{-1}$
	P1	2.2×10^{-12}	11.76	1.4×10^{-10}
	P2	3.0×10^{-12}	51.85	$\approx10^{-9}$
	P3	1.2×10^{-12}	17.39	$\approx10^{-8}$
	P4	1.9×10^{-12}	30	9.2×10^{-9}
	P5	3.1×10^{-12}	20.64	2.0×10^{-8}
	P6	1.9×10^{-12}	20.25	$\approx10^{-8}$
	P7	5.0×10^{-11}	3.67	2.3×10^{-8}
	P8	2.3×10^{-8}	3.98	1.9×10^{-8}

lacetylene were used as purchased from Aldrich Co. Additionally, 1,4-diethynylbenzene,[20] 1,3-diethynylbenzene,[20] 2-ethylnythiophene,[21] 5,5′-dibromo-2,2′-bithienyl[22], 5,5′-dibromo-3,3′-dimethyl-2,2′-bithienyl[22] and 4,4′-diethynylbiphenyl[23] were prepared according to published procedures. Elemental analyses of C and H were done by M-H-W Laboratory, Phoenix, AZ. Differential Scanning Calorimetry was performed on a Perkin-Elmer DSC 7 Series Thermal Analysis System at a heating rate of 40°C/min under a steady flow of nitrogen. The IR spectra (KBr pellets) were recorded on a Perkin-Elmer model 599. A Bruker Ac-250 MHz spectrometer was used to record ^{1}H-NMR spectra. A Perkin-Elmer Lambda 5 Spectrophotometer was used to take UV-visible spectra. A Hewlett-Packard 5995 Gas Chromatograph/Mass Spectrometer was used to record MS data at 70 eV. Electrical conductivity was measured with a four-point probe on pressed pellets.[24]

PREPARATION OF MONOMERS

2,5-Bis(2-thienylethynyl)thiophene (M1)

A 250 ml 3-necked round bottomed flask equipped with a reflux condenser, magnetic stirrer and nitrogen inlet was charged with 100 ml dry triethylamine, 42.8 mg (22.8 mmole) copper(I) iodide, 4.839 g (20 mmole) 2,5-dibromothiophene and 4.86 g (45 mmole) 2-ethynylthiophene. Nitrogen was then bubbled through for 20 minutes. To the stirred mixture 71.6 mg (.06 mmole) tetrakis(triphenylphosphine)palladium(O) was added under a constant flow of nitrogen. The resulting mixture was heated with stirring at 95°C for 12 hours. After cooling to room temperature, the precipitated triethylamine hydrobromide was filtered off. The filtrate was diluted with 200 ml of chloroform and washed 3 times with water, then dried over anhydrous magnesium sulfate. The organic solvents were removed under reduced pressure. The crude product was purified by column chromatography using 10% ethyl acetate/hexane as eluent and 3.55 g (60%) of pure M1 was collected as a yellow solid, m.p. 117–118°C (lit 116–118°C)[25], UV (λ_{max}, ($CHCl_3$); 366.6 nm, ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.00–7.03 (m, 2H) δ 7.14 (s, 2H), δ 7.29–7.33 (m, 4H). Anal. calcd. for $C_{16}H_8S_3$, C calcd. 64.83%; found 65.05%; H calcd. 2.72%, found 2.96%. M.S. m/e: 45 (14%), 97 (2%), 145 (7%), 148 (8%), 219 (5%), 264 (3%), 296 (M^+, 100%), 297 ($M^+ + 1$, 21%), 298 ($M^+ + 2$, 15%).

2,5-Bis-(2-phenylethynyl)thiophene (M2)

It was prepared as earlier described[25] for M1, however, 4.839 g (20 mmole) 2,5-dibromothiophene and 2.247 g (45 mmole) phenylacetylene were used. The crude product was purified by column chromatography using 10% ethyl acetate/hexane as the elutant and 4.2 g (75%) of pure M2 was collected as a pale yellow solid, m.p. 86–87°C; UV (λ_{max}, $CHCl_3$): 348.8 nm; ^1H NMR (250 MHz, $CDCl_3$): δ 7.15 (s, 2H), δ 7.335–7.34 (m, 6H), δ 7.503–7.524 (m, 4H). Anal. Calcd. for $C_{20}H_{12}S$; C calcd. 84.47%, found 84.60%; H calcd. 4.25%, found 4.50%; M.S. m/e: 203 (100%), 203 (69%), 204 (70%), 284 (M^+, 50%), 285 (M^+ +1, 10%), 286 (M^+ +2, 32%).

5,5′-Bis-(2-phenylethynyl)-2,2′-bithienyl (M3)

The procedure was carried out as described above. However, 6.48 5 (20 mmole) 5,5′-dibromo-2,2′bithienyl and 2.247 g (45 mmole) phenylacetylene were used. The mixture was heated with stirring at 95°C for 24 hours. The crude product was purified by column chromatography using 10% ethyl acetate/hexane as eluent and 5.49 g (75%) of pure M3 was collected as a yellow solid, m.p. 165°C; UV (λ_{max}, $CHCl_3$) 384.7 nm; ^1H NMR (250 MHz, $CDCl_3$): δ 7.07 (d, AB system, J = 3.82 Hz, 2H), δ 7.17 (d, AB system, J = 3.82 Hz, 2H), δ 7.30–7.40 (m, 6H), δ 7.47–7.54 (m, 4H). Anal. Calcd. for $C_{24}H_{14}S_2$: C calcd. 78.65%, found 78.70%; H calcd. 3.85%, found 4.00%. M.S. m/e: 83 (34%), 266 (25%), 366 (M^+, 100%), 367 (M^+ +1, 25%), 368 M^+ +2, 12%).

5,5′-Bis-(2-phenylethynyl)-3,3′-dimethyl-2,2′-bithienyl (M4)

The procedure was carried out as described previously. However, 7.04 g (20 mmole) 5,5′-dibromo-3,3′-dimethyl-2,2′-bithienyl and 2.247 g (45 mmole) phenylacetylene were used.

The crude product was purified by column chromatography using 10% ethyl acetate/hexane as the eluent and 4.73 g (60%) pure M4 was collected as a yellow solid, m.p. 114–115°C; UV (λ_{max}, $CHCl_3$) 337.8 nm; ^1H NMR (250 MHz, $CDCl_3$: δ 2.20 (s, 6H), δ 7.10 (s, 2H), δ 7.31–7.36 (m, 6H), δ 7.48–7.53 (m, 4H). Anal. Calcd. for $C_{26}H_{18}S_2$: C calcd. 79.19%, found 78.96%; H calcd. 4.57%, found 4.57%. M.S. m/e: 197 (7%), 377 (4%), 378 (2%), 379 (3%), 380 (1%), 394 (M^+, 100%), 395 (M^+ +1, 32%), 396 (M^+ +2, 14%), 397 (M^+ +3, 3%).

1,4-Bis-(2-thienylethynyl)benzene (M5)

The procedure was carried out as described previously, but 2.53 g (20 mmole) 1,4-diethynylbenzene and 7.33 g (45 mmole) 2-bromothiophene were used.

The crude product was purified by column chromatography using 10% ethyl acetate/hexane as eluent and 4.35 g (75%) of pure M5 was collected as a pale yellow solid, m.p. 204–205°C (lit 197.5–199°C)[26], UV (λ_{max}, $CHCl_3$) 339.8 nm; ^1H NMR (250 Mhz, $CDCl_3$): δ 7.01–7.04 (m, 2H), δ 7.29–7.33 (m, 4H), δ 7.49 (s, 4H). Anal. Calcd. for $C_{18}H_{10}S_2$: C calcd. 74.45%, found 74.35%; H calcd. 3.47%, found 3.59%; M.S. m/e: 145 (30%), 245 (25%), 290 (M^+, 100%), 291 (M^+ +1, 55%), 292 (M+ +2, 30%).

1,3-Bis-(2-thienylethynyl)-benzene (M6)

The procedure was carried out as described previously but 2.53 g (20 mmole) 1,3-diethynylbenzene and 7.33 g (45 mmole) 2-bromothiophene were used.

The crude product was purified by column chromatography using 10% ethyl acetate/hexane as eluent and 4.64 g (80%) of pure M6 was collected as colorless solid, m.p. 162–163°C; UV (λ_{max}, $CHCl_3$) 305.6 nm; ^1H NMR (250 Mhz, $CDCl_3$): δ 7.00–7.03 (m, 2H), δ 7.28–7.36 (m, 5H), δ 7.45–7.49 (m, 2H), δ 7.67–7.68 (m, 1H). Anal. Calcd. for $C_{18}H_{10}S_2$: C calcd. 74.45%, found 74.25%; H calcd. 3.47%, found 3.62%. M.S. m/e: 45 (14%), 145 (9%), 243 (4%), 290 (M^+, 100%), 291 (M^+ +1, 20%), 292 (M^+ +2, 10%).

4,4′-Bis-(2-thienylethynyl)biphenyl (M7)

The procedure was carried out as described previously. However, 4.04 g (20 mmole) 4,4′-diethynylbiphenyl and 7.335 g (45 mmole) 2-bromothiophene were used.

The crude product was purified by column chromatography using chloroform as the eluent and 4.39 g (60%) of pure M7 was collected as a yellow solid. m.p. 220–222°C (decomposed); UV (λ_{max}, $CHCl_3$) 337.4 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 7.025 (t, 2H), δ 7.315 (dd, 4H), δ 7.59 (s, 8H). Anal. Calcd for $C_{24}H_{14}S_2$: C calcd. 78.65%, found 78.42%; H calcd. 3.85%, found 4.00%. M.S. m/e: 277 (38%), 278 (19%), 279 (4%), 322 (57%), 323 (15%), 332 (3%), 338 (14%), 340 (13%), 366 (M^+, 100%), 367 (M^+ +1, 27%), 368 (M^+ +2, 14%).

4,4′-Bis-[2-(3-methyl-2-thienylethynyl)]-biphenyl (M8)

The procedure was carried out as described previously. However, 4.04 g (20 mmole) 4,4′-diethynylbiphenyl and 7.965 g (45 mmole) 2-bromo-3-methylthiophene were used.

The crude product was purified by column chromatography using 30% ethyl acetate/hexane as the eluent and 5.56 g (70%) of pure M8 was collected as a yellow solid, m.p. 166–168°C; UV (λ_{max}, $CHCl_3$), 344.4 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 2.42 (s, 6H), δ 6.885 (d, AB system, ^JAB = 5 Hz, 2H), δ 7.20 (d, AB systems, ^JAB = 5 Hz, 2H), δ 7.60 (s, 8H). Anal. Calcd. for $C_{26}H_{18}S_2$: C calcd. 79.19%, found 79.32%; H calcd. 4.57%, found 4.70%. M.S. m/e: 394 (M^+ +1, 100%), 395 (M^+ +1, 33%) 396 (M^+ +2, 14%).

1,3,5-Tris-2-thienylethynylbenzene (M9)

The procedure was carried out as described previously. However, 1.47 g (10 mmole) 1,3,5-triethynylbenzene and 5.705 g (35 mmole) 2-bromothiophene were used.

The crude product was purified by column chromatography using chloroform as the eluent and 1.58 g (40%) of pure M9 was collected as a yellow solid, m.p. 230–232°C (decomposed); UV (λ_{max}, $CHCl_3$) 309.6 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 7.025 (t, 3H) δ 7.32 (dd, 6H), δ 7.61 (s, 3H). Anal. Calcd. for $C_{24}H_{12}S_3$: C calcd. 72.69%, found 72.73%; H calcd. 3.05%, found 3.18%. M.S. m/e: 322 (100%), 323 (20%), 366 (10%), 393 (10%), 396 (M^+, 90%), 397 (M^+ +1, 20%), 398 (M^+ +2, 10%).

PREPARATION OF POLYMERS

Poly-2,5-(1,4-phenylethynyl)thiophene (P1)

To a mixture of 316 mg (2.5 mmole) of 1,4-diethynylbenzene, 605 mg (2.5 mmole) 2,5-dibromobenzene, NEt_3 (3 ml), and toluene (40 ml) was added 29.3 mg (0.025 mmole) of $(PPh_3)_4Pd(O)$ and 10 mg (0.025 mmole) of CuI. After stirring for 2 hours under reflux, the reaction mixture was poured into excess MeOH. The precipitate was separated by filtration and the solid was washed repeatedly with MeOH. It was dried under vacuum to obtain P1. After removing the toluene-soluble fraction of P1 by extraction with hot toluene using a soxlet extractor the yellow-greenish solid was dried under vacuum to yield 240 mg of

P1 (found C, 77.64; H, 3.74; Br 7.85). From the toluene extract 224 mg of low molecular weight of P1 were obtained.

Poly-2,5-(1,4-phenylethynyl)-3-methylthiophene (P2)

The procedure was carried out as described above, using 316 mg (2.5 mmole) of 1,4-diethynylbenzene and 637 mg (2.5 mmole) of 2,5-dibromo-3-methylthiophene to obtain 300 mg of P2 (found C, 76.89; H, 3.73; Br 7.39%) and 230 mg of low molecular weight P2.

Poly-5,5′-(1,4-phenylethynyl)-2,2′-bithienyl (P3)

The procedure was carried out as described previously, using 316 mg (2.5 mmole) of 1,4-diethynylbenzene and 810 mg (2.5 mmole) of 5,5′-dibromo-2,2′-bithienyl to obtain 500 mg of P3 (found C, 69.54; H, 3.04; Br, 9.55%) and 190 mg of low molecular weight P3.

Poly-5,5′-(1,4-phenylethynyl)-3,3′-dimethyl-2,2′-bithienyl (P4)

The procedure was carried out as described previously, using 316 mg (2.5 mmole of 1,4-diethynylbenzene and 880 mg (2.5 mmole) of 5,5′-dibromo-3,3′-dimethyl-2,2′-bithienyl to obtain 470 mg of P4 (found C, 71.47; H, 3.76; Br, 7.31%) and 260 mg of low molecular weight P4.

Poly-2,5-(4,4′-diethynylbiphenyl)thiophene (P5)

The procedure was carried out as described previously, using 505 mg (2.5 mmole) of 4,4′-diethynylbiphenyl and 613 mg (2.5 mmole) of 2,5-dibromothiophene to obtain 200 mg of P5 (found C, 74.01; H, 3.83; Br, 5.70%) and 310 mg of low molecular weight P5.

Poly-2,5-(4,4′-diethynylbiphenyl)-3-methylthiophene (P6)

The procedure was carried out as described previously, using 505 mg (2.5 mmole) of 4,4′-diethynylbiphenyl and 638 mg (2.5 mmole) of 2,5-dibromo-3-methylthiophene to obtain 320 mg of P6 (found C, 77.43; H, 4.00; Br, 6.38%) and 240 mg of low molecular weight P6.

Poly-5,5′-(4,4′-diethynylbiphenyl)-2,2′-bithienyl (P7)

The procedure was carried out as described previously, using 505 mg (2.5 mmole) of 4,4′-diethynylbiphenyl and 810 mg (2.5 mmole) of 5,5′-dibromo-2,2′-bithienyl to obtain 440 mg of P7 (found C, 74.03; H, 3.60; Br, 8.46%) and 380 mg of low molecular weight P7.

Poly-5,5′-(4,4′-diethynylbiphenyl)-3,3′-dimethyl-2,2′-bithienyl (P8)

The procedure was carried out as described previously, using 505 mg (2.5 mmole) of 4,4′-diethnylbiphenyl and 880 mg (2.5 mmole) of 5,5′-dibromo-3,3′-dimethyl-2,2′-bithienyl to obtain 550 mg of P8 (found C, 72.00; H, 3.98; Br, 7.85%) and 390 mg of low molecular weight P8.

CONCLUSIONS

The monomers and polymers of thiophene substituted acetylenes can be synthesized in high yields using a Pd-catalyzed C-C coupling reaction. The monomers possess, as expected a high λ_{max} value due to their extended conjugated electron system. However, a simple and straightforward relationship between the exhibited λ_{max} values, as was found earlier by us for poly(thiophenes), was not apparent. The polymers derived of these monomers are of low molecular weight and are in the undoped as well as iodine doped state insulators.

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