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Synthesis and Characterization of Copolymers of Aniline and Thiophene

D. W. Polis, C. L. Young, M. R. McLean, and L. R. Dalton*

Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1062

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ABSTRACT: Reaction of dibromothiophenes with *p*-phenylenediamines under Ullmann condensation conditions proceeds to form copoly(thiophenediyl-1,4-diaminophenylenes). The reaction temperature had a dramatic effect on the structure of the final product. Thermal decomposition of the thiophene rings led to a fused ladder type polymer with limited solubility. Detailed thermal, spectroscopic, and analytical data afforded the complete characterization as well as established the means of distinguish between fused and unfused systems. Soluble fractions of the polymers allowed characterization of the molecular weight distribution, which gave insight into the morphology of the materials. Preliminary measurements (degenerate four-wave mixing) have demonstrated appreciable third-order nonlinear optical responses ($\chi^{(3)}$ of approximately 4×10^{-10} esu) and high laser damage thresholds (4 GW/cm^2).[1]

Introduction

In recent years there has been much interest in fully conjugated polymers with favorable physical properties. The materials must have atmospheric and thermal stability, processibility, and desirable electrical properties. Fortunately, it is possible to tailor the molecular structure of organic materials to fit the necessary physical requirements. Applications including optical wave guide devices, sensor protection, and optical computing have prompted much research.[2]

We have previously studied polyquinoxaline ladder polymers formed by condensation of substituted quinones with aromatic tetramines.[3] The tractability of such materials through functionalization is essential in maintaining film formability without loss in molecular weight. The optical properties of other conjugated polymers such as BBL and polyaniline can be dramatically altered by doping, and this may be a means of enhancing linear and nonlinear optical characteristics in the visible region.[4,5] It is essential to minimize absorption for wave guide and optical computing applications because of the need to optimize response at lower laser intensities, which require greater optical path lengths.

The synthesis of the fused ladder structures is complicated by the necessity for complete cyclization of the prepolymers.[6] However, there are some elegant ways around this problem. For example, the oxidative thermal annealing of polyacrylonitrile has been shown to proceed to an almost graphitic matrix.[7] We chose to study a copolymeric system of aniline and thiophene for two reasons. There is precedence for thermal decomposition of the diaminothiophenediyl ring by ring opening and/or radical mechanisms, leading to a fully fused system.[8-11] Also, the absorption band edge could be easily controlled by protonic doping. Secondly, if rigid-rod materials were formed, high third-order nonlinear optical susceptibilities would be expected, in accordance with polyaniline and polythiophene.

Experimental Section

Chemicals. The monomers used in preparation of the polymers are shown in Figure 1. 2,5-Dibromothiophene (T1), 3,4-dibromothiophene (T2), *p*-phenylenediamine (D1), and 2,5-dichloro-*p*-phenylenediamine (D2) were supplied by Aldrich Chemical Co., while 3-methyl-2,5-dibromothiophene (T3) was supplied by Alfa products (Morton-Thiokol Co.). The 2,5-dibromothiophene, 3,4-dibromothiophene, and 3-methyl-2,5-dibromothiophene were purified by vacuum distillation (105 °C at 1 mmHg, 123 °C at 0.5 mmHg, and 125 °C at 0.5 mmHg, respectively). The 2,5-dichloro-*p*-phenylenediamine was recrystallized from aqueous ethanol (mp 161–163 °C), and *p*-phenylenediamine was vacuum sublimed (100 °C, 1 mmHg) to give white needles (mp 143–144 °C). Copper(I) iodide was supplied by Lancaster Synthesis Ltd., and all solvents were furnished by J. T. Baker Chemical Co.

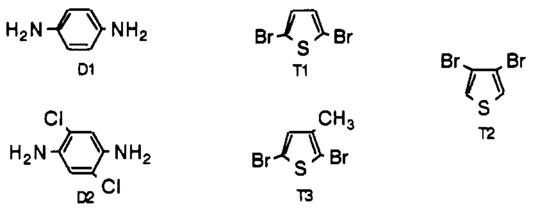
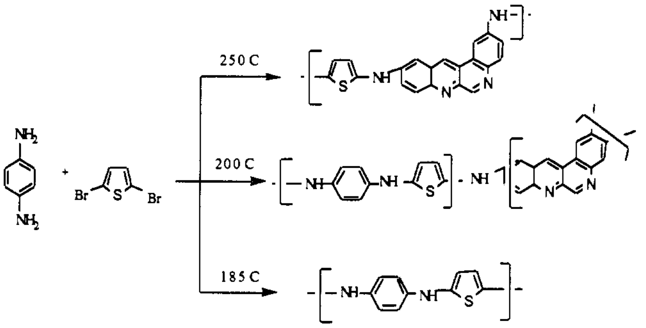


Figure 1. Structure of monomers.

Scheme I



Synthesis of Polymers. The synthetic scheme is illustrated in the synthesis of copoly(thiophenediyl-1,4-diaminophenylene) (Scheme I). 2,5-Dibromothiophene (4.84 g, 0.02 mol) was placed in a Paar pressure reaction bomb along with *p*-phenylenediamine (2.16 g, 0.02 mol), sodium carbonate (2.12 g, 1 equiv), dimethyl sulfoxide (30 mL), and a trace of copper(I) iodide (0.01 molar %, ca. 4 mg). The bomb was assembled and flushed for 20 min with a stream of ultrapure (99.999%) hydrogen and then pressurized to 100 psi with hydrogen. Hydrogen was used to minimize oxidation of aromatic amine nitrogen or thiophene sulfur.

The bomb was then rapidly heated to 185 °C with stirring, and the temperature was maintained for 20 h. After cooling and release of pressure, the reaction contents were poured into 500 mL of 10% aqueous hydrochloric acid to remove salts. After filtration and washing with 100 mL of 10% aqueous ammonium hydroxide, the crude material was transferred to a Soxhlet

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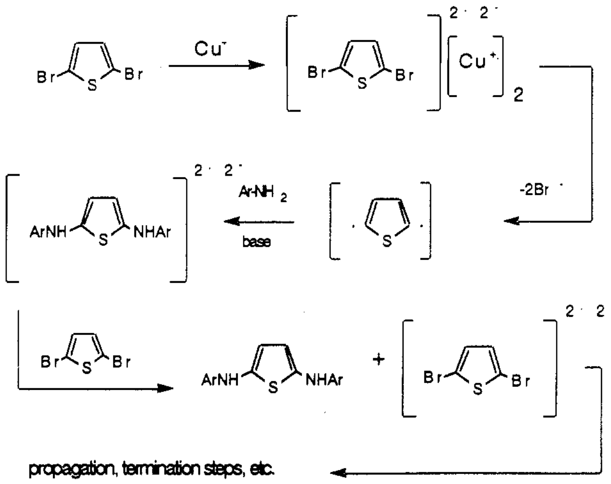
Scheme II



extractor and extracted first with water and finally with ethanol until the extracts were colorless. The resulting polymer required careful drying at 0.1 mmHg at 120 °C for at least 24 h to remove all bound water (see Figure 7). Yield 3.38 g (89.9%). Elemental analyses are shown in Table III.

Infrared Spectra. The infrared spectra (KBr pellets) were recorded on a Perkin-Elmer Model 1760 Fourier transform infrared spectrophotometer with a nominal resolution of 4 cm^{-1} and a total of 16 scans.

UV Spectroscopy. UV–vis spectroscopy of DMF solutions was performed on a Perkin-Elmer Lambda 4C UV/Vis spectrophotometer with a slit width of 1 (0.5-nm resolution), a scan speed of 120 nm/min, and a scan range from 190 to 900 nm.

Thermal Measurements. A Perkin-Elmer TGA7 thermogravimetric analyzer was used to investigate the thermal stability of the materials between ambient and 900 °C. A nitrogen purge was used to exclude oxidative decompositions.

A Perkin-Elmer TMA7 thermomechanical analyzer was used to investigate the expansion and penetration properties of the materials. The decomposition thresholds from TGA measurements dictated the upper temperature limit for the mechanical measurements. Pellets were pressed with a Perkin-Elmer infrared pellet maker and a Carver laboratory press (20 000 psi). Appropriate samples were cut from the resulting pellets for both expansion and penetration studies. Scan rates were varied from 5 to 20 °C/min, with a load of 10 mN for expansion studies and 50 mN for penetration studies.

A Perkin-Elmer DSC7 differential scanning calorimeter was used to investigate the thermodynamic behavior of the materials. The upper temperature limit was set below the decomposition temperature using TGA data to avoid damage to the sample holder. Scanning rates from 5 to 20 °C/min showed almost identical results.

Gel Permeation Chromatography (GPC). A Hewlett-Packard Model 1090 liquid chromatograph with diode array detection at 280 nm was used for all GPC characterizations. The solvent was HPLC-grade DMF (Aldrich) with a HP Plgel column (5 μm, 10^4 Å). Flow rate was constant at 1 mL/min, and molecular weight distribution was standardized against polystyrene with known molecular weights (10^3–10^6 amu).

Elemental Analyses. All elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Duplicate analyses were performed for better accuracy and in most cases showed less than a 0.5% difference in analytical parameters.

Results and Discussion

The synthesis of the copoly(thiophenediyl-1,4-diaminophenylenes) proceeded readily at 185 °C. The expected dianilino adduct was formed by nucleophilic attack of arylamine on a bis-organometallic intermediate. The proposed reaction mechanism for the reaction is shown in Scheme II. Since the formation of the organometallic intermediate involves an $\mathrm{S_{NR}1}$ reaction, radical decomposition mechanisms of the thiophene ring system become conceivable. In fact, on close examination of the elemental analyses for polymers formed at higher temperature, it became apparent that indeed thiophene rings were undergoing decomposition. This is illustrated in Table I, which shows the percent sulfur for several different polymers formed at different temperatures.

The lower than expected sulfur content (based on a 1:1 alternating copolymer) can be explained by thermal decomposition of the thiophene ring system. This is reasonable in terms of the thermal lability of sulfur in other nitrogen-containing thiophenes.[10] Interestingly, the reaction pressure was also responsible for a marked difference in sulfur content (polymers **3** and **4**). Since polymer **3** had a low sulfur content (low-pressure conditions) and polymer **4** had a high sulfur content (high-pressure conditions), it is apparent that pressure effectively inhibits thiophene ring decomposition for the 2,5-dibromothiophene polymers (2,5 systems). This suggests loss of a small molecule, which could be H_2S and/or H_2. Actually, loss of H_2S from the diaminothiophenediyl ring and H_2 from between aromatic and thiophene rings is essential in drawing the more fused structures presented.

There is a difference in behavior between 2,5 systems and polymers of 3,4-dibromothiophene (3,4 systems). Under pressurized conditions it appears that 2,5 systems undergo partial thiophene oligomerization at 200 °C, while 3,4 systems showed partial thiophene oligomerization at 185 °C. It has been shown that bis-organometallic reagents of thiophene readily polymerize with dibromothiophenes in the presence of a variety of catalysts.[12] Perhaps at 200 °C, in the presence of Cu^+, the 2,5 systems are sufficiently activated to undergo oligomerization with bromothiophene (dibromothiophene or thiophene terminated end group), whereas in 3,4 systems this process occurs at the lower temperature of 185 °C.

The solubility of the materials was minimal. Table II lists the solubility characteristics for several of the materials. In general, fused materials showed a lower solubility in common solvents such as DMF, *N*-methylpyrrolidinone (NMP), and dimethyl sulfoxide (DMSO). Strong acids such as methanesulfonic acid (MSA), trifluoromethanesulfonic acid (TFMSA), sulfuric acid, and trifluoroacetic acid (TFA) seemed to be suitable for obtaining more concentrated solutions and subsequent casting into brittle films. For polymers **1**, **2**, **3**, **5**, and **6** films could be removed from glass slides by soaking in 10% aqueous HF solution; however, isolation of large pieces of free-standing film was only obtainable for polymers **2** and **3**. Optical-quality composite films in poly(vinyl alcohol) were cast from TFA solutions for polymers **1**, **2**, **5**, and **7**. Viscosity measurements were not possible due to low solubility (nominally 10^{-5} M).

We have classified the materials into fused and unfused systems based on the sulfur content in the resulting polymer (except polymer **7**; vide infra). Generalized structures are presented in Scheme I. The remaining discussion of the data will attempt to elucidate the structures of the polymers, based on an in-depth examination and analysis of the data.

Elemental Analysis. The elemental analyses for the polymers are presented in Table III. Empirical formulas were determined by back-calculation, and actual formulas were deduced by elemental balance. For example, for each sulfur or bromine seen in the calculated empirical formula there had to be a corresponding four carbon atoms (or five for T2 polymers). Similarly, for each two

Table I
Sulfur Content and Identification of Polymers

polymer	D1[a]	D2[a]	T1[a]	T2[a]	T3[a]	temp, °C	% S (exptl/calcd)
1	×	—	×	—	—	250	8.06/17.03
1b	×	—	× (0.7)[c]	× (0.3)	—	250	3.06/17.03
2	×	—	—	×	—	250	1.46/17.03
2b	×	—	× (0.3)[c]	× (0.7)	—	250	2.97/17.03
3[b]	×	—	×	—	—	200	3.91/17.03
4	×	—	×	—	—	200	23.35/17.03
5	×	—	—	×	—	185	24.54/17.03
6	×	—	×	—	—	185	15.99/17.03
7	×	—	—	—	×	185	18.53/15.85
8	—	×	—	—	×	185	13.21/11.82
9	—	×	×	—	—	185	12.66/12.47

[a] Monomers shown in Figure 1. [b] At 1 atm of nitrogen. [c] 0.7 and 0.3 refer to molar percentages with respect to diamine.

Table II
Solubility of Polymers[a]

	solvent[b]				
polymer	DMF	DMSO	H_2SO_4	TFMSA	TFA
1	ss	ss	ss		
2	ss	s	s		
3		ss	s	s	ss
5	ss[c]				ss
6	ss[c]				i
7	ms[c]	ms		s	ss
8	i[c]	i			i
9	ss[c]				i

[a] ss = slightly soluble; ms = moderately soluble; s = soluble; i = insoluble. [b] Solvent at 80 °C. [c] Insoluble residue determined gravimetrically: polymer **5** = 78%; polymer **6** = 69%; polymer **7** = 52%; polymer **8** = 96%; polymer **9** = 83%.

nitrogen atoms there had to be a corresponding six carbons (and two chlorine atoms for D2 polymers). Hydrogen was then added to balance the valency requirements.

Residue and water content were seen in all polymers. It should be noted that combustion problems resulting in residue and deviations of the elemental analyses from theoretical calculations are common in fused polymers of nitrogen.[13] Water content was measured from TGA traces of polymers exposed to air for long periods of time. As will be shown, it was very difficult to produce moisture-free materials. Polymers **1**–**4** were not analyzed for residue; the difference from 100% in the elemental analysis was taken to be water plus residue.

Figure 2 shows the empirically deduced structure for several of the polymers. Polymer **7** proved to be a special case with ring closure and fusion of the polymer into the structure shown. Loss of epi hydrogen between the methyl group of the thiophene moiety and the aromatic ring is feasible, leading to the formation of the six-membered ring, which then aromatizes.[11]

Interestingly, the analogous ring closure with the 2,5-dichloro-1,4-diaminobenzene/3-methylthiophene polymer (polymer **8**) does not occur. In this case approximately half the chlorine is lost and replaced with hydroxy. This is supported by a broad band at 3300 cm^{-1} (Figure 4e) in a carefully dried sample. We hypothesize that water liberated from the condensation reaction quickly hydrolyzes chlorine from the forming polymer, the phenolic residue being very effective in inhibiting radical formation of adjacent methylthiophenes.

The molecular weight range based on bromine content showed the materials to be of low molecular weight (2000–5000 amu); however, additional evidence from GPC analysis suggested higher molecular weights. Figure 3 shows a GPC trace for a typical polymer system; the molecular weight distribution appeared bimodal. Considering the sulfur loss and the free radical mechanism, it is very likely that the polymers are cross-linked.

A second, high molecular weight peak in the GPC trace is due not to a significantly higher molecular weight species but to a more fully cross-linked polymer. The fully cross-linked species had a particle size larger than the cavities of the GPC resin and appeared as a high molecular weight fraction. A polystyrene equivalent molecular weight of main GPC fraction was between 15 000 and 40 000 amu. It is likely that 2000–5000-amu oligomers are cross-linked, giving a higher molecular weight species, as demonstrated in the GPC traces.

Infrared Spectra. The infrared spectra for several of the polymers are shown in Figure 4. For comparison, the spectra for pristine polythiophene and the polyaniline oligomer emeraldine (undoped) are presented.[12,14] As can be envisioned, the polymers synthesized contain absorptions for both the aniline and thiophene polymers. In fact, the broad bands seem to be an almost superposition of the parent polymer absorptions. This is most clearly indicated in polymer **7**, which shows the characteristic benzenoid C–C stretch at 1520 and 1618 cm^{-1} in addition to bands at 1424 and 1492 cm^{-1}, which are characteristic of C–C stretching in substituted thiophenes.

UV–vis Spectra. There is a clear difference in the UV–vis spectra for materials that were classified as fused or unfused (polymer **7** also displayed fused character). As can be seen from Figure 5, with increasing fusion absorption bands become broader and begin tailing into the near-IR, as expected for increasingly conjugated systems. The absorption maximum at 265 nm was evident in both fused and unfused materials, with unfused materials displaying two shoulders at 288 and 298 nm. The fused materials, including polymer **7**, showed a side band at approximately 325 nm trailing out to 800 nm.

For polymers **5**–**9**, absorption coefficients were calculated in DMF solutions (Table IV). It is interesting to note that materials formed from 2,5-dichloro-1,4-diaminobenzene (polymers **8** and **9**) demonstrated approximately an order of magnitude difference in absorption coefficient, in contrast with the two polymers formed from 3-methyl-2,5-dibromothiophene, which are not distinct. This indicates that the absorption at 265 nm is primarily due to benzenoid absorption and not to thiophene absorption.

Thermal Analysis. The thermal stabilities of the materials were excellent. Heat stabilities of up to ca. 500 °C for fused materials and up to ca. 250 °C for unfused materials were noted. Figure 6 shows TGA traces for several of the polymers. Two important aspects should be noted. First, the materials are very hygroscopic, as is evident from a polymer sample that was carefully dried and then allowed to stand exposed to the atmosphere for 2 days

Table III
Elemental Analysis of Polymers

	% C	% H	% N	% S	% Br	% Cl	% O[a]	ash
polymer 1 found	58.67	3.38	11.45	8.06	5.51			12.93[b]
$C_{10}H_{5.97}N_{1.95}S_{0.54}Br_{0.12}\cdot H_2O$ + 2.93% ash	58.62	3.93	13.34	8.59	4.76		7.84	2.93
polymer **1b** found	64.36	3.66	11.70	3.06	8.95			8.25[b]
$C_{10}H_{5.55}N_{2.04}S_{0.18}Br_{0.18}\cdot 0.63H_2O$ + 3.00% ash	62.52	3.58	14.85	3.09	7.70		5.26	3.00
polymer 2 found	63.94	4.23	15.32	1.46	4.60			10.45[b]
$C_{10}H_{6.43}N_{2.04}S_{0.10}Br_{0.10}\cdot 0.92H_2O$ + 2.39% ash	63.97	4.44	15.23	1.74	4.34		7.88	2.39
polymer **2b** found	63.76	3.86	12.17	2.97	3.91			13.33[b]
$C_{10}H_{5.48}N_{1.73}S_{0.19}Br_{0.09}\cdot 0.77H_2O$ + 4.00% ash	64.91	3.83	13.10	3.33	4.15		6.68	4.00
polymer 3 found	62.37	5.06	15.12	3.91	3.15			10.39[b]
$C_{10}H_{8.86}N_{2.0}S_{0.21}Br_{0.07}\cdot 1.03H_2O$ + 2.00% ash	62.52	5.73	14.58	3.58	2.97		8.63	2.00
polymer 4 found	53.59	2.98	8.74	23.35	2.73			8.60[b]
$C_{10}H_{7.03}N_{1.30}S_{1.52}Br_{0.07}\cdot 0.75H_2O$ + 3.00% ash	54.53	3.91	8.29	22.15	2.63		5.48	3.00
polymer 5 found	52.38	2.66	8.14	24.54	9.32		0.90	1.46
$C_{10}H_{6.92}N_{1.28}S_{1.54}Br_{0.25}\cdot 0.11H_2O$ + 1.74% ash	54.55	3.28	8.16	22.40	9.30		0.87	1.46
polymer 6 found	52.28	3.32	9.78	15.99	6.33		10.01	1.72
$C_{10}H_{7.5}N_{1.67}S_{1.26}Br_{0.21}\cdot 1.1H_2O$ + 1.72% ash	51.66	4.25	10.04	17.25	7.16		7.93	1.72
polymer 7 found	59.74	3.59	11.52	18.53	1.52		3.76	1.34
$C_{11}H_{6.50}N_{1.67}S_{1.18}Br_{0.04}\cdot 0.47H_2O$ + 1.34% ash	61.43	3.49	10.90	17.82	1.48		3.53	1.34
polymer 8 found	48.58	2.89	10.46	13.21	3.88	11.21	7.71	2.06
$C_{11}H_{9.2}N_{1.9}S_{1.1}Br_{0.1}Cl_{0.9}O_{1.1}\cdot 0.3H_2O$ + 2.1% ash	49.38	3.67	10.02	12.61	2.86	11.41	8.00	2.06
polymer 9 found	48.44	2.43	9.51	12.66	3.25	11.11	9.31	3.29
$C_{10}H_{7.23}N_{1.91}S_{1.06}Br_{0.10}Cl_{0.75}O_{1.17}$ + 3.29% ash	48.01	2.91	10.72	13.63	3.40	10.55	7.48	3.29

[a] By difference. [b] Residue and oxygen by difference.

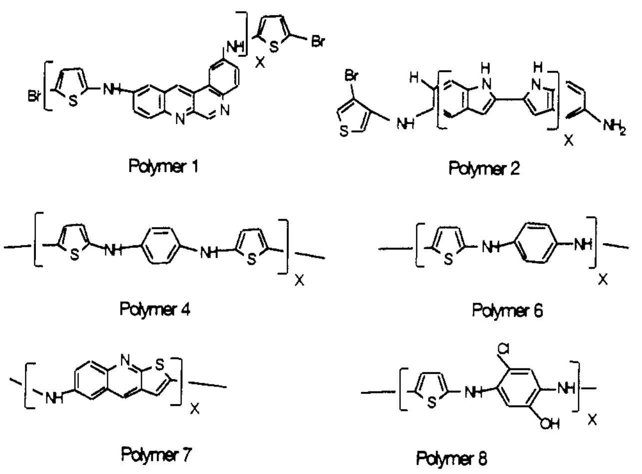


Figure 2. Structure of polymers.

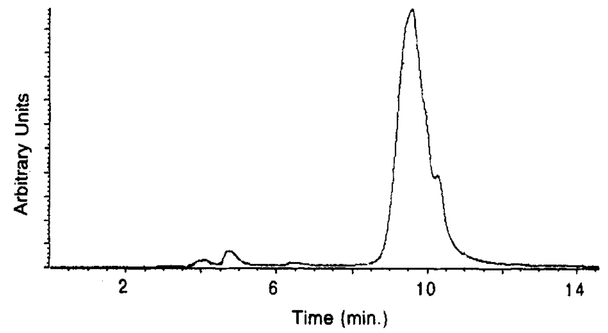


Figure 3. GPC trace for aniline–thiophene copolymers.

(Figure 7). Second, the structural differences in fused and unfused materials is evident from TGA traces alone. Fused materials showed much higher heat resistance, whereas unfused materials showed the onset of decomposition at ca. 250 °C.

To gain an understanding of the decomposition mechanism, we employed DSC analysis. Figure 8 shows a typical DSC trace for a fused and unfused material. There exists an endothermic transition for fused materials at ca. 250 °C. This is attributed to the consumption of the thiophene ring in the furnace. The unfused materials showed only a strong endothermic curve starting at ca. 200 °C. Lastly, we noted a purely exothermic trailing of the DSC for fused materials at temperatures between 250 and 500 °C (the significant decomposition temperature). We believe this to be the reconstitution of the matrix by bond rearrangement, resulting in a more fused graphitic-like material. This is supported by lack of structure in IR analysis of materials heated above 500 °C.

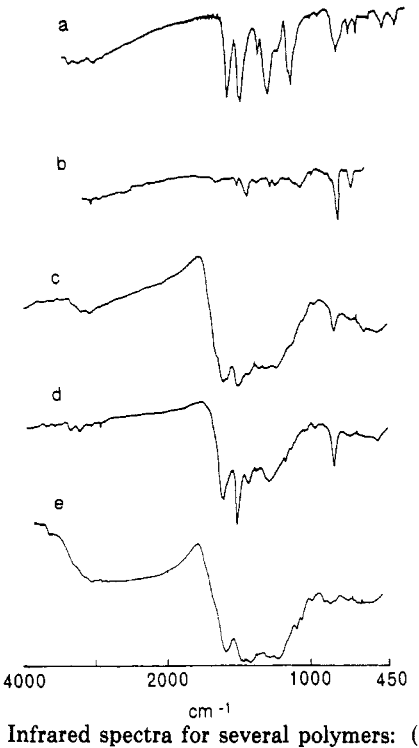


Figure 4. Infrared spectra for several polymers: (a) emeraldine; (b) polythiophene; (c) polymer **6**; (d) polymer **7**; (e) polymer **9**.

Thermal mechanical analyses supplied another clue in distinguishing between fused and unfused materials. Figure 9 shows TMA traces for two sets of fused and unfused materials. Coefficients of thermal expansion are presented in Table V. In unfused materials the coefficient of thermal expansion is approximately 4 times greater than in fused materials. This result immediately suggests a pattern of expansion. The unfused materials displayed more of a "spaghetti" type nature, while the fused materials appeared more rigid, resisting the tendency to

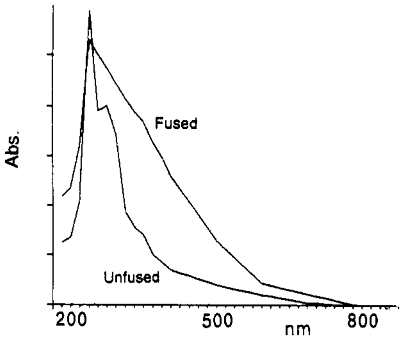


Figure 5. UV–vis spectra for fused (polymer 1) and unfused (polymer 6) systems.

Table IV
Absorption Coefficients for Polymers

polymer	concn, M × 10^{-5}	A(265 nm)	absorption coeff (×10^3)
5	1.42	0.270	19.0
6	2.65	0.938	35.4
7	3.45	1.08	31.4
8	29.9	1.21	4.04
9	19.5	0.480	2.46

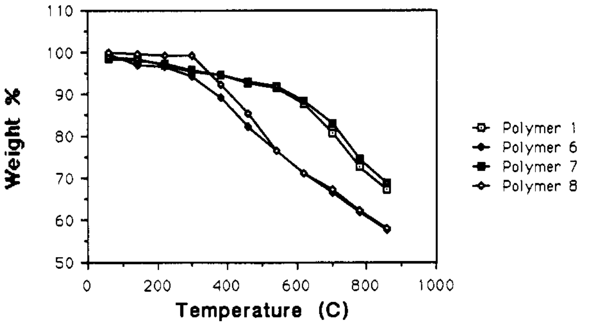


Figure 6. TGA traces for fused and unfused polymers.

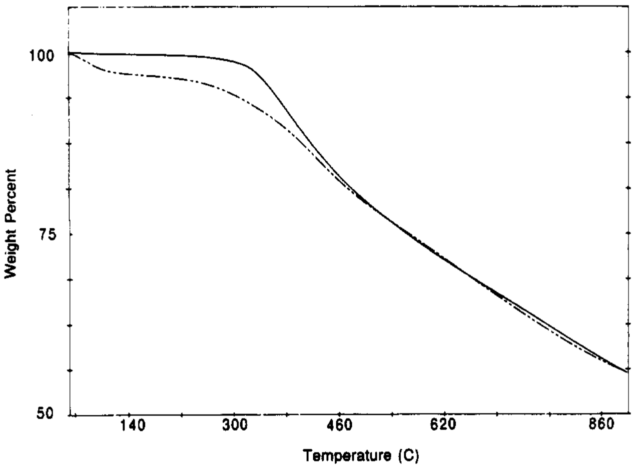


Figure 7. Evidence of hygroscopicity (polymer 6).

expand and slide over each other.

The appearance of two separate expansion coefficients for polymers **3** and **4** provides more evidence for the thermal degradation of thiophene rings leading to a fused matrix at temperatures below 200 °C. It is apparent that the intermediate structure between fused and unfused displays properties similar to each.

Magnetic Properties. A complete discussion of the electronic and magnetic properties of the materials is presented in the following paper.[15] We will mention that magnetic and electron spin resonance characterizations did follow the same trends and strongly supported the fused and unfused structures presented.

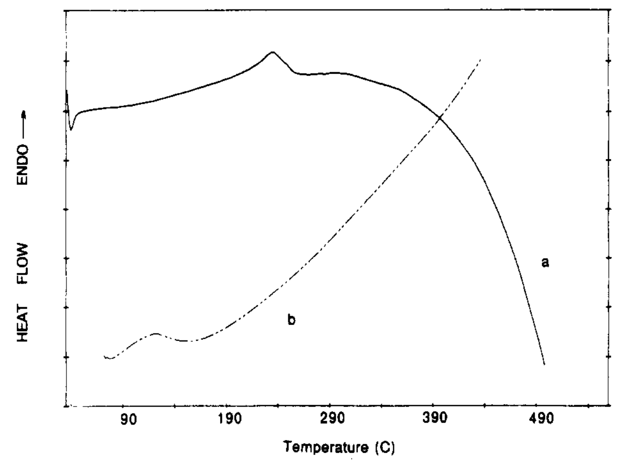


Figure 8. DSC analysis of polymers: (a) polymer 1 (fused); (b) polymer 6 (unfused).

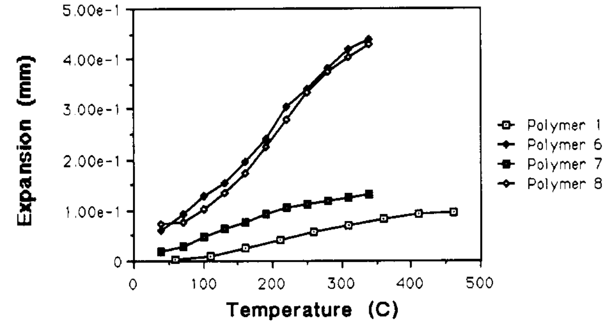


Figure 9. TMA traces for fused and unfused polymers.

Table V
Coefficients of Thermal Expansion

polymer	coeff, mm/C × 10^{-4}
1	1.08 (60–450 °C)
1b	1.23 (60–410 °C)
2	1.07 (60–460 °C)
2b	2.16 (60–460 °C)
3	6.03 (60–120 °C), 0.89 (130–250 °C)
4	8.07 (60–110 °C), 2.47 (120–250 °C)
5	4.48 (60–250 °C)
6	4.65 (60–250 °C)
7	1.48 (60–220 °C)
8	4.24 (90–250 °C)
9	3.89 (90–250 °C)

Conclusions

Polymeric materials are readily synthesized by condensation of aromatic diamines with dibromothiophenes under Ullmann conditions. By varying reaction parameters, one can synthesize either fused or unfused materials, which can be monitored by various analytical techniques. The absolute structure of the materials has been deduced by correlation of elemental analysis, detailed thermal analysis, and spectroscopic data. The materials displayed limited solubility; however, sufficient concentrations allowed casting into neat films and composite films in poly(vinyl alcohol) which both displayed third-order nonlinear optical properties.[1]

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Registry No. 1 (copolymer), 121753-88-6; **1b** (copolymer), 126724-55-8; **2** (copolymer), 126724-56-9; **7** (copolymer), 126724-57-0; **8** (copolymer), 126724-58-1; **9** (copolymer), 126724-59-2.

Electronic and Magnetic Character of Aniline–Thiophene Copolymers

C. L. Young, D. W. Polis, A. N. Bain, L. S. Sapochak, and L. R. Dalton*

Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1062

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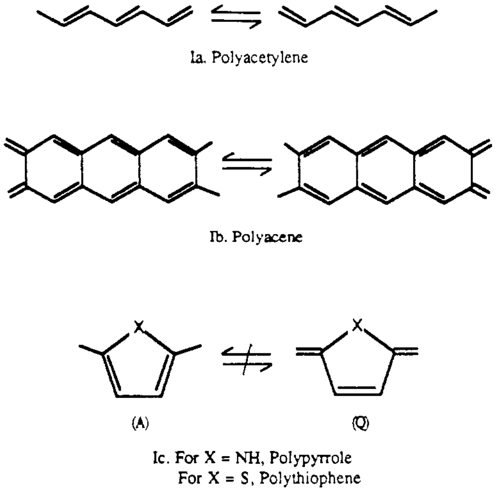
ABSTRACT: The condensation of 2,5-dibromothiophenes or 3,4-dibromothiophene with 1,4-diaminophenylenes under Ullmann conditions yielded a series of aniline–thiophene copolymers. Elevated reaction temperatures resulted in loss of the sulfur by decomposition of the thiophene ring. Lower reaction temperatures produced materials of a more rigid rod character with retention of the thiophene ring. The influence of the sulfur heteroatom was clearly visible in the optical and ESR spectra. Magnetic susceptibility measurements on the materials produced from the 2,5-dibromothiophenes (the 2,5-copolymers) revealed anomalous temperature-independent paramagnetism, or Pauli susceptibilities (χ^{Pauli}), which are usually associated with metals. Comparison of the materials produced at higher reaction temperatures with those formed at lower temperatures indicates that the sulfur atom strongly interacts with spin-carrying defects, thereby determining the electronic and magnetic character of these novel polymeric systems.

Introduction

Heteroatomic polymers have been the subject of serious investigation for the past decade.[1] Many of these materials are electrically conductive upon doping and are under investigation for their potential usefulness in the production of nonlinear optical (NLO) devices.[2] The role of a heteroatom in the origin of such anomalous electronic and optical properties remains ill-defined. Polymers without heteroatomic influences, such as polyacetylene (PA) and polyacene (PAc), have degenerate bond phases and intrinsically higher symmetry (Scheme I). Systems exhibiting this degeneracy are predicted to support solitonic defects,[3] which may occupy a mid-bandgap electronic state and provide spin character that is detectable by electron spin resonance (ESR) techniques.

Heterocyclic systems such as polythiophene (PT)[4] and polypyrrole (PP),[5] as seen in Scheme Ic, have nondegenerate bond phases, and the midgap states are polaronic in nature. These systems can be synthesized and doped electrochemically, have relatively small band gaps (E_g(PT) = 2.1 eV, E_g(PP) = 3.0 eV), and are comparatively more stable and processible than other nonheteroatomic systems such as PA. The nondegenerate bond phases are quinoidal (Q) and aromatic (A), with the quinoidal being the higher energy conformation.[6] Another well-characterized heteroatomic polymer, polyaniline (PAni), also has both quinoidal and aromatic (benzoidal) character.[7]

Scheme I



Ic. For X = NH, Polypyrrole
For X = S, Polythiophene

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