Polyarylenealkenylenes and Polyheteroarylenealkenylenes XVIII.[†]
Polycondensation of 5-Methylfuran-2-carbaldehyde—
An Easy Route to Electrically Conductive Materials

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ABSTRACT: The synthesis of dark brown poly(2,5-furan-diylvinylene) (1) *via* aldol condensation reaction of 5-methylfuran-2-carbaldehyde as an one pot reaction yields an organic semiconductor which has long-lasting stability in the presence of air and water (tested over 10 years). Decolorization (decomposition) was observed only under long-time illumination. The reaction products were characterized by IR-, ^{1}H NMR-, mass-spectrometry and elemental analysis. Polymer 1 can be oxidized (doped) with Lewis acids such as iodine, AsF_5 and $FeCl_3$. The values of the electrical conductivity range from $10^{-8}\,S\,cm^{-1}$ for the pristine material (activation energy $E_a = 0.36\,eV$) up to $1.5 \times 10^{-2}\,S\,cm^{-1}$ for the AsF_5 complex ($E_a = 0.10\,eV$). Pristine oligomeric material is fusible and can be used to improve the mechanical properties of the polymeric material.
   KEY WORDS   Electrical Conductive Polymers / Poly(2,5-furan-diylvinylene) / Organic Semiconductor / Polymeric Organic Semiconductor / Doped Organic Semiconductor /

As already known from studies on polyacetylene,[1] the challenge and difficulty is in combining good electrical conductivity with stability and easy handling in the presence of air.[2] Normally, conducting polymers cannot be processed from the melt, therefore fusible and "soluble polymers are on the way."[3] Aromatic ring systems in the main chain of electrically conducting polymeric materials increase their stability.[4,5] One approach to combine high stability with high electrical conductivity is to introduce aromatic ring systems into the polymer chain.[6)] Some methods of synthesizing conjugated polymeric vinylenes have been reported.[7-12] To get processable materials, precursor-routes have been developed.[13-17]

In this paper we depict some modified ways of the polycondensation of 5-methylfuran-2-carbaldehyde yielding poly(2,5-furan-diylvi-nylene) (1). Materials can be obtained which are partly soluble in different organic solvents, fusible, and can be oxidized with Lewis acids such as iodine, AsF_5 or $FeCl_3$.

These materials belong to the series of intensively investigated conjugated polymers with heterocycles such as poly(2,5-thienylene-vinylene).[9,12,15,16]

EXPERIMENTAL

Synthesis   of 1 via Aldol Self-Condensation Reactions of 5-Methylfuran-2-carbaldehyde with a Basic Catalyst

2.000 g (18.2 mmol) 5-methylfuran-2-carbaldehyde (2) and 1.010 g (18.2 mmol) powdered KOH were stirred into 100 ml *N,N*-dimethylformamide (DMF) under N_2 at 80°C for 5 h. After cooling to room temperature, the

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[†] Part XVII: G. Koßmehl and M. Samandari, *Makromol. Chem.*, **186**, 1565 (1985).

dark reaction product was filtered into an extraction vessel, exhaustively extracted with water, ethanol and acetone and finally dried over P_4O_{10} under vacuum. The resulting product (**1-B, 1**) was a black powder which does not melt up to 350°C. The yield was 1.105 g (66% of the theoretical yield). The density of **1-B, 1** was found between 1.29 and 1.47 g cm^{-3}.

1-B, 1 $(C_6H_4O)_n$ $(92.1)_n$
  Calcd: C, 78.25%; H, 4.38%.
  Found: C, 75.57%; H, 4.59%.
  $[(C_6H_4O)_{0.82}(C_6H_6O_2)_{0.18}]_n$ $(95,3)_n$
  Calcd: C, 75.57%; H, 4.58%.

About one third of **1-B, 1** is soluble in *N,N*-dimethylacetamide (DMAc) giving an intensively violet colored solution. **1-B, 1** is soluble in the starting material **2**.

Corresponding to the above mentioned conditions, 32.00 g (0.291 mol) **2** and 16.16 g (0.291 mol) KOH pellets were stirred in 100 ml DMF at 80°C for 5 h. The reaction mixture was distilled under vacuum to remove the solvent. Afterwards, the reaction product was exhaustively extracted with water and finally dried over P_4O_{10} under vacuum at 80°C. The resulting material was a dark brown powder (**1-B, 2**). The yield was 26.24 g (98%).

The density is between 1.43 and 1.48 g cm^{-3}.

1-B, 2 $[(C_6H_4O)_{0.72}(C_6H_6O_2)_{0.28}]_n$ $(97,3)_n$
  Found: C, 74.13%; H, 5.50%.
  Calcd: C, 74.22%; H, 4.73%.

There are far more soluble parts in this material in comparison to **1-B, 1** and it can be fused (at about 150°C).

When **1-B, 2** was heated up to 300°C for 10 min (**1-B, 2tt**) the elemental analysis yielded:

1-B, 2tt $[(C_6H_4O)_{0.86}(C_6H_6O_2)_{0.14}]_n$ $(94,5)_n$
  Found: C, 76.15%; H, 4.82%.
  Calcd: C, 76.13%; H, 4.53%.

The obtained material was hard and brittle. It does not melt up to 350°C and is not soluble in organic solvents. The density is between 1.12 and 1.23 g cm^{-3}.

Thermally Induced Aldol Self-condensation Reaction Forming **1**

The polycondensation reaction can also be induced thermally by heating **2** at temperatures of between 80°C and 160°C. The reaction vessel should be open to allow the water formed during the polycondensation reaction to evaporate. The reaction time varies considerably compared with the experimental conditions from 30 min up to several days. As **2** also evaporates, the yield of the thermal polycondensation reaction varies widely, in temperature and in the preparative conditions (up to 90%). With increasing reaction temperature and time, the solubility of the obtained material decreases and the melting temperature increases. For example:

2.000 g (18.2 mmol) **2** are placed in a petri dish and left in a desiccator over KOH-pellets at 90°C for 6 days. The result is 0.55 g of a black material (**1-T**) (33%). The melting temperature is nearly 60°C.

1-T $[(C_6H_4O)_{0.62}(C_6H_6O_2)_{0.38}]_n$ $(98,9)_n$
  Found: C. 72.72%; H, 4.81%.
  Calcd: C. 72.77%; H, 4.84%.

The reaction product dissolved in methanol can be separated by HPLC methods into 4% of **2**, 42% dimer, 36% trimer, 14% tetramer, and 4% pentamer. The shortest oligomers (*n* between 1 and 3) can be separated by sublimation, forming high viscous liquids or yellowish to orange colored needles. The melting temperature for such mixtures of oligomers is around 30°C or even lower.

The electronic spectrum of **1-T** dissolved in DMF shows following absorption peaks: an absorption at 282 nm, a strong absorption at 385 nm (λ_{max}) and a big shoulder at 460 nm.

The ^{1}H-NMR spectrum (CDCl$_3$) of a sample containing predominant *trans*-1-(5-formyl-2-furyl)-2-(5-methyl-2-furyl)ethylene (dimer) shows signals at $\delta = 2.33$ (s; 3H; –CH$_3$), 6.05 (d; 1H; furan), 6.38 (d; 1H; furan), 6.45 (d; 1H; furan), 6.74/7.14 (dd; 2H; –CH=CH–), 7.25 (d; 1H; furan), 9.62 (s; 1H, –CHO).

The electronic spectrum of this sample

dissolved in DMF has a strong absorption at 385 nm (λ_{max}).

Aldol Self-condensation Reaction with an Acidic Catalyst Forming 1

100 ml 37% by weight HCl was added to 2.000 g (18.2 mmol) of **2** and the solution stirred at room temperature for 5 days. A brown microcrystalline powder was obtained with a melting temperature of about 110°C. The reaction product is soluble or partly soluble in different organic solvents, but not in water. The yield is 1.27 g (76%).

The density is between 1.48 and 1.58 g cm^{-3}.

1-A $[(C_6H_4O)_{0.62}(C_6H_6O_2)_{0.38}]_n$ $(98,9)_n$
  Found: C, 72.76%; H, 5.59%.
  Calcd: C, 72.77%; H, 4.84%.

IR (KBr): 3020 (w; HAr), 2925 (w; –CH–), 1670 m; –CHO), 1600—1570 (s; furan), 1440 (s, furan), 1020 (vs; furan), 940 (vs; –CH = CH–), trans), 780 cm^{-1} (s; furan, 2,5-disubstituted).

Densities of the Polymeric Samples

To measure the density, the samples were suspended in mixtures of diethylether/bromoform with differing densities. This is not simple in all cases because of dissolving or forming/destructing charge transfer complexes with the sample material.

Oxidation (Doping) of Polymer 1

Oxidation with Iodine. Oxidation with iodine was performed in the gas phase. A sample of the polymer **1-B, 1** (100 mg) and about 5 g of iodine were placed into a desiccator and left at room temperature for 24 h. Afterwards, the sample was dried over KOH under vacuum for one week. Finally 175 mg of the oxidized polymer (oxidized by iodine) were obtained.

The density is between 1.53 and 1.67 g·cm^{-3}.

1-B, 1, a $(C_6H_4O \cdot I_{1.32})_n$
  Calcd: C, 27.76%; H, 1.55%; I, 65.54%.
  Found: C, 27.78%; H, 1.70%; (I, 64.51%).
The oxygen content is calculated in relation to the carbon and hydrogen content. The iodine content is calculated as the difference to 100%.

Oxidation with AsF$_5$. Samples of polymer **1-B, 1** were treated with gaseous AsF$_5$ at a pressure of 600 mbar for 66 h. Then the samples were stored for 24 h under vacuum together with KOH. The density of the AsF$_5$ treated sample (**1-B, 1, b**) is between 1.53 and 1.63 g cm^{-1}.

1-B, 1, b $((C_6H_4O) \cdot (AsF_6)_{0.995})_n$
  Calcd:
    C, 25.71%; H, 1.43%; AsF$_6$,67.15%.
  Found:
    C, 23.49%; H, 2.60%;(AsF$_6$, 67.14%).

The oxygen content is calculated in relation to the carbon and hydrogen content. The AsF$_6$ content is calculated as the difference to 100%.

1-B, 1, b was stirred with water for 5 min and then dried under vacuum over KOH for 24 h giving **1-B, 1, c** with a density between 1.53 and 1.59 g cm^{-1}.

1-B, 1, c $((C_6H_4O) \cdot (AsF_6)_{0.15})_n$
  Calcd:
    C, 59.64%; H, 3.31%; AsF$_6$, 23.8%.
  Found:
    C, 56.53%; H, 3.96%; (AsF$_6$ 23.8%).

1-B, 1, c was also stirred for 5 min with 25% aqueous ammonia solution and dried under vacuum over KOH for 24 h forming **1-B, 1, d**.

1-B, 1, d $((C_6H_4O) \cdot (AsF_6)_{0.07})_n$
  Calcd:
    C, 68.18%; H, 3.79% AsF$_6$, 12.88%.
  Found: C, 63.48%; H, 4.41%; N, 1.82%
    (AsF$_6$, 12.69%)

Oxidation with FeCl$_3$. **1** can also be oxidized with FeCl$_3$. Polymer **1-B, 1** was suspended in varying solutions of FeCl$_3$ in 50 ml CH$_3$CN and stirred at ambient temperature for 18 h.

Sample	Mass (polymer 1)	Mass (FeCl$_3$)	Molar ratio ($x:y$)	Yield
1-B, 1, e	94.0 mg	146.4 mg	1 : 0.88	96.2 mg
1-B, 1, f	92.5 mg	284.0 mg	1 : 1.74	111.0 mg
1-B, 1, g	92.2 mg	406.2 mg	1 : 2.50	109.3 mg

The obtained chemical compositions are:

1-B, 1, e $((C_6H_4O)\cdot(FeCl_4)_{0.065})_n$
  Calcd: C, 68.67%; H, 3.84%; Cl, 8.76%.
  Found: C, 62.38%; H, 3.69%; Cl, 8.92%.
1-B, 1, f $((C_6H_4O)\cdot(FeCl_4)_{0.12})_n$
  Calcd: C, 62.23%; H, 3.48%; Cl, 14.69%.
  Found: C, 58.55%; H, 3.44%; Cl, 18.44%.
1-B, 1, q $((C_6H_4O)\cdot(FeCl_4)_{0.16})_n$
  Calcd: C, 58.25%; H, 3.26%; Cl, 18.34%.
  Found: C, 50.38%; H, 2.98%; Cl, 18.44%.

DISCUSSION

The aldol self-condensation reaction of **2** can be catalysed with a base or an acid; or the reaction can be conducted thermally, in close relation to the well-known mechanism of the aldol-addition reaction.[18] Polyaddition of **2** followed by dehydration (*trans*-elimination) would form in the ideal case polymer **1** with only *trans*-vinylene units:
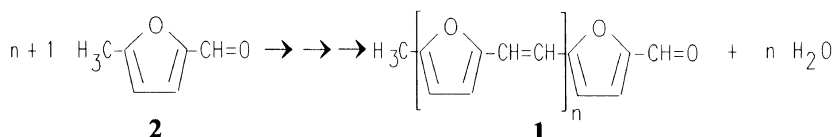
Ideal Formula of polymer **1**

In reality complete condensation reaction does not occur as it is known with simple aliphatic aldehydes. From the elemental analysis of the samples we know that the dehydration is not complete. The sample **1-B, 1** in average contains about five vinylene groups and one hydroxyethylene group besides of furan-diyl units in the chain. This means relatively good addition reaction followed by dehydration forming vinylene groups (ideal structure of polymer **1**). By mass spectrometric measurements of polymer **1-B, 1** (350°C; 80 eV) oligomers up to the decamer (939 u) are found as volatile constituents of the reaction mixture. Apart from these molecular peaks, typical fragments which result from the loss of CH_2 (14 u), CH_3 (15 u), CO (28 u), and CH_3CO (43 u) are also found. MS under equal conditions for parts of **1-B, 1** which are soluble in ethanol, give peaks up to the nonameric vinylene (847 u).

A typical IR-spectrum confirms the structure of the synthesized material as poly(2,5-furan-diylvinylene) with some remaining hydroxy-ethylene groups instead of vinylene groups: One can see three peaks for the furan system (1570—1600, 1440, and 1020 cm^{-1}), one peak for the 2,5-disubstituted furan system (780

cm^{-1}), the CH wagging absorption for the *trans*-vinylene units (940 cm^{-1}), the C=O absorption for carboxaldehyde end groups (1670 cm^{-1}), a weak absorption for secondary alcoholic units of –CHOH–CH$_2$– (3400 cm^{-1}), and the absorption for CH, CH$_2$, and CH$_3$ groups (2925 cm^{-1}). The occurrence of alcoholic groups can be understood because of partly Aldol addition reaction without elimination of water.

The electronic spectrum of polymer **1-B, 1** pressed as KBr pellets shows in the visible range two typical absorption peaks: a strong absorption at 525 nm (λ_{max}) with a shoulder at 595 nm, and a characteristic spectrum of the soluble part of polymer **1-B, 2** dissolved in DMF (Figure 1).

In a Debye–Scherrer X-ray diffraction pattern of **1-B, 1** one finds reflections due to distances of 318.7, 370.8, 395.2, 486.1, and 553.9 ppm.

It is very difficult to provide information on the molecular weight of **1**. The calculated values for C and H of the elemental analyses on the basis of an ideal structure with end groups according to formula **1**, gives an average virtual condensation degree of $n = 5.5$ for **1-B, 1** and a virtual average condensation degree of
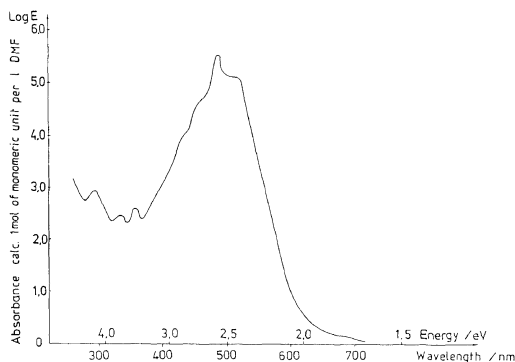
Figure 1. Electronic spectrum of polymer **1-B, 2** dissolved in DMF.

$n = 3.6$ for **1-B, 2**, because of incomplete elimination of water, from the addition product of the reaction, meaning the presence of alcoholic groups instead of vinylene groups. This indicates a lower polycondensation degree.

The ^{1}H NMR spectrum of the soluble part of **1-B, 2** shows considerable quantities of secondary alcoholic units ($-CHOH-CH_2-$) as well as *trans*-vinylene units ($-CH=CH-$): the ^{1}H NMR spectrum taken in $CDCl_3$ contains signals at $\delta = 1.7$—1.9 (d; OH), 2.49 (s; $-CH_2-$), 4.78 (m; $-CH-$), 6.5—7.3 (m; furan system; $-CH=CH-$). Analogous results were also produced by ^{13}C NMR studies for **1-B, 1**, taken in the solid state. We get signals at 14 ($-CH_3$, $-CH_2-$, weak), 56 ($-CH_2O-$, weak), 114 ($-CH=CH-$, strong), 153 (-furan-, strong), and 173 ppm (-CHO, weak). Moieties with secondary alcoholic units [$-C_6H_4O-CH(OH)-CH_2-$, addition product] have the same number of atoms as units bearing end groups ($-CH_3$ and $-C_6H_4O-CHO$, see formula). Therefore, the values found for C and H in the elemental analysis agree with calculated values for C and H for a lower chain length (ideal conjugated structure with end groups as in the formula for **1**). The average chain length of the material **1** is most probably at least double or even more than calculated on this basis because it contains a considerable amount of secondary alcoholic units. One other observation should

also be mentioned. If, for example the sample **1-B, 2** is heated up to temperatures higher than its melting temperature for 10 min, the material again solidifies. Afterwards, it does not melt up to 350°C and is mostly insoluble. The IR spectra of samples treated in this way yield a weaker absorption for the carboxaldehyde end group and for hydroxy groups, compared to the untreated sample. A sample of **1-B, 2** was heated up to 300°C for 10 min. The values for carbon of the elemental analysis show a higher virtual degree of condensation ($n \cong 7$). Thermogravimetrical measurements of **1-B, 2** under nitrogen show stability up to 300°C. The sample weight decreases slowly to 95% at 380°C. At 380°C and 460°C a drastic loss of weight occurs.

Summarizing our results on the molecular weight we find molecular masses up to the decameric vinylene as volatile parts of the polymeric materials. We believe that also higher molecular masses are present. The vapor osmotic measurements of the soluble part of **1-B, 1** in DMAc shows molecular masses around 400 u in average.

With regard to the stability of polymer **1**, no differences were found between a freshly synthesized sample and one which had been left in air for ten years; neither in the IR-spectrum, nor in the electrical conductivity. Also, the treatment with water with subsequent drying did not influence the properties of polymer **1**. A ^{13}C NMR spectrum in the solid state (CPMAS) of a 12 years old sample (comparable to **1-B, 1**) yield only two signals at 152 ppm ($-CH=CH-$) and 113 ppm (furan).

In order to measure the electrical conductivity of the powdery polymer **1**, pressed samples were taken to be measured by a "sandwich" method. The conductivity was measured directly within the press under a pressure of 1.08×10^5 N cm^{-2} ($= 1500$ kp cm^{-3}) as a standard condition.[19] The temperature of the measurement was changed by simply heating up and cooling down the sample under pressure (about 150°C to ambient
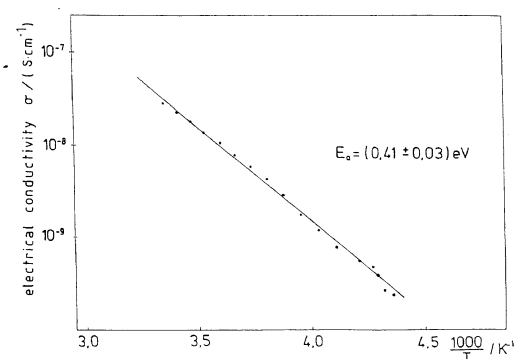
temperature).[20]

Samples of the thermally polymerized material **1-T** were melted on thin cover glass and contacted. The electrical conductivities of these samples were measured under vacuum by the 2-point method. The samples were either cooled down by liquid nitrogen or solid CO_2 and then heated up to determine the activation energy E_a, which is calculated by

$$\sigma = \sigma_0 \exp(-E_a/2kT)$$

The dc-conductivity of polymer **1-B, 1** is $\sigma_{298K} = 2.1 \times 10^{-8}\,S\,cm^{-1}$ and the activation energy $E_a = 0.36\,eV$ (sandwich method; pressure $1.08 \times 10^5\,N\,cm^{-2}$).

For **1-T**, dc-conductivity is $\sigma_{298K} = 5 \times 10^{-8}$

Figure 2. Temperature dependence of the electrical conductivity for the pristine material **1-T**.

$S\,cm^{-1}$ and $E_a = 0.41\,eV$ (measured by the 2-point method without pressure; see Figure 2).

Analogous to other well-studied polymers poly(2,5-furan–diylvinylene) has been oxidized by various Lewis acids as acceptors. During oxidation secondary alcoholic units can eliminate water forming vinylene units. So for calculating the elemental analysis the ideal formula of polymer **1** $(C_6H_4O)_n$ is used.

The values of the electrical conductivity for pristine and oxidized samples of polymer **1** are given in Table I.

The values of the electrical conductivity of **1** is comparable to the values given for pristine poly(2,5-thiophenediylvinylene)[7] with $\sigma_{298K} = 3.8 \times 10^{-8}\,S\,cm^{-1}$ and for polyacetylene with $10^{-8}\,S\,cm^{-1}$.

It is interesting to note that an increase of the average condensation degree from the value of the thermally polymerized material **1-T** to that of **1-B, 1**, practically does not change either the electrical conductivity nor the activation energy. Only **1-B, 2tt** portrays a drastic lower value of the electrical conductivity, (comparing the density of **1-B, 2** with **1-B, 2tt** a decrease of the density from $\rho_{av.} = 1.45$ to $\rho_{av.} = 1,17$ $g\,cm^{-3}$ can be observed). In comparable materials (**1-B, 1**; **1-B, 2**; **1-B, 2tt**) the density portrays an influence on the electrical conductivity (see also Table I). Regarding these

Table I. Values of the electrical conductivity of pristine and oxidized samples of **1**

Sample no.	Formula		σ_{298K} $S\,cm^{-1}$	E_a eV
1-B, 1	$[(C_6H_4O)_{0.82}(C_6H_6O_2)_{0.18}]_n$	$(95,3)_n$	2.1×10^{-8}	0.36
1-B, 2	$[(C_6H_4O)_{0.72}(C_6H_6O_2)_{0.28}]_n$	$(97,3)_n$	3.0×10^{-8}	0.33
1-B, 2tt	$[(C_6H_4O)_{0.86}(C_6H_6O_2)_{0.14}]_n$	$(94,5)_n$	2.0×10^{-10}	0.02
1-T	$[(C_6H_4O)_{0.62}(C_6H_6O_2)_{0.38}]_n$	$(98,9)_n$	5.0×10^{-8}	0.41
1-A	$[(C_6H_4O)_{0.62}(C_6H_6O_2)_{0.38}]_n$	$(98,9)_n$	4.0×10^{-11}	0.05
1-B, 1a	$(C_6H_4O \cdot I_{1.32})_n$		1.2×10^{-3}	0.48
1-B, 1b	$[(C_6H_4O) \cdot (AsF_6)_{0.995}]_n$		1.5×10^{-2}	0.05
1-B, 1c	$[(C_6H_4O) \cdot (AsF_6)_{0.15}]_n$		6.0×10^{-3}	0.19
1-B, 1d	$[(C_6H_4O) \cdot (AsF_6)_{0.071}]_n$		7.0×10^{-10}	0.40
1-B, 1e	$[(C_6H_4O) \cdot (FeCl_4)_{0.065}]_n$		2.7×10^{-3}	0.23
1-B, 1f	$[(C_6H_4O) \cdot (FeCl_4)_{0.12}]_n$		1.7×10^{-3}	0.34
1-B, 1g	$[(C_6H_4O) \cdot (FeCl_4)_{0.16}]_n$		1.3×10^{-3}	0.34

effects, for good electrical conductivity and easy handling it is better not to remove oligomeric parts of **1** from the material, so that they both together can work as a system of softener and conductive filler.

REFERENCES

1. A. G. MacDiarmid, *Ann. Rev., Phys. Chem.*, **33**, 443 (1982).
2. J. L. W. Chien, "Polyacetylene," Academic Press, New York, 1984, chapter 7, p 250.
3. P. Calvert, *Nature*, **327**, 371 (1987).
4. R. L. Elsenbaumer and L. W. Shacklette, "Phenylene-Based Conducting Polymers," in T. A. Skotheim, Ed., "Handbook of Conducting Polymers," Vol. 1, M. Dekker, New York, N.Y., 1986, p 213.
5. G. B. Street, "Polypyrrole: From Powders to Plastics," in T. A. Skotheim, Ed., "Handbook of Conducting Polymers," Vol. 1, M. Dekker, New York, N.Y., 1986, p 265.
6. M. Haertel, G. Koßmehl, G. Manecke, W. Wille, D. Woehrle, and D. Zerpner, *Angew. Makromol. Chem.*, **29/30**, 307 (1973).
7. G. Koßmehl, M. Härtel, and G. Manecke, *Makromol. Chem.*, **131**, 15 (1970).
8. G. Koßmehl and M. Samandari, *Makromol. Chem.*, **186**, 1565 (1985).
9. G. Koßmehl, *Ber. Bunsenges. Phys. Chem.*, **83**, 417 (1979).
10. G. Koßmehl, "Semiconducting and Conducting Polymers with Aromatic and Heteroaromatic Units," in T. A. Skotheim, Ed., "Handbook of Conducting Polymers," Vol. 1, Marcel Dekker, New York, N.Y., 1986, p 351.
11. S. Antoun, D. R. Gagnon, F. E. Karasz, and R. W. Lenz, *J. Polym. Sci., C*, **24**, 503 (1986).
12. K. Y. Jen, R. Richard, H. Eckhardt, and R. L. Elsenbaumer, *Polym. Mater. Sci. Eng.*, **56**, 49 (1987).
13. R. A. Wessling and R. G. Zimmermann, US-Patent 3,401,152 (1968).
14. R. A. Wessling and R. G. Zimmermann, US-Patent 3,706,677 (1972).
15. S. Antoun, D. R. Gagnon, F. E. Karasz, and R. W. Lenz, *J. Polym. Sci., C*, **24**, 503 (1986).
16. Kwan-Yue Jen, T. R. Jow, and R. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 1113 (1987).
17. P. L. Brun, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, *Nature*, **356**, 47 (March, 5, 1992).
18. N. L. Allinger, M. P. Cava, D. C. de Jongh, C. R. Johnson, N. A. Lebel, and C. L. Stevens, "Organic Chemistry," Worth Publishers Inc., New York, 1973, p 500.
19. J. Danhaeuser and G. Manecke, *Makromol. Chem.*, **84**, 238 (1965).
20. G. Koßmehl and G. Manecke, *Chem.-Ing.-Techn.*, **39**, 1041 (1967).