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Synthesis, Characterization, and Stability of High Molecular Weight Poly(thiophene-2,5-diyl-1,2-dimethoxyvinylene)

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ABSTRACT: The new polymer poly(thiophene-2,5-diyl-1,2-dimethoxyvinylene) was synthesized by a benzoin condensation of thiophene-2,5-dicarboxaldehyde to poly(2,5-thienylene-1-oxo-2-hydroxyethylene) ($M_w \sim 1 \times 10^6$, pd ~ 13), followed by O-alkylation using dimethyl sulfate. A side reaction of the benzoin condensation step leading to dimethyl-2,5-thiophenedicarboxylate can be avoided by using cyclohexanol as the solvent. The O-alkylation, including the workup, has to be performed under nitrogen protection to counteract the degradation of the polymer by air under the influence of light. A mechanism is proposed for the oxidative degradation of this poly(thiophene-2,5-diylvinylene) derivative and other poly(arylenevinylenes). Conductivity and thermal properties of the new polymer are given.

Introduction

Polymers that combine a high degree of conjugation with a high degree of substitution are of interest, because they may combine semiconductivity with solubility. Several alkyl-substituted poly(thiophene)s have been reported to be soluble, highly conducting, and environmentally stable on acceptor doping.[1] This stabilizing effect can be increased by incorporating alkoxy substituents on the conjugated system. At the same time, these electron-donating substituents can reduce the bandgap and the ionization potential such that it becomes possible to dope the polymers with milder oxidizing reagents.[2] Moreover, these charged polymers will be more stable than the nonsubstituted analogues.[3]

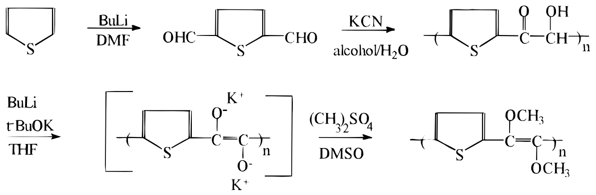
This project reports the synthesis of a soluble poly(thiophene-2,5-diylvinylene) (PTV), dimethoxy-substituted on the vinylene linkages. The synthetic route chosen is shown in Scheme 1. The influence of the solvent and reaction time on the molecular weight will be discussed. Also reported is the thermal stability and the stability toward ozone and photooxidation.

Synthetic Aspects

Polymerization. Thiophene-2,5-dicarboxaldehyde was prepared according to Feringa et al.[4] in a yield of 80%. The precursor polymer, poly(2,5-thienylene-1-oxo-2-hydroxyethylene) was synthesized using the benzoin condensation. An unexpected side reaction occurred; dimethyl-2,5-thiophenedicarboxylate was formed in significant amounts in a Cannizzaro-like reaction. To prevent this, the reaction time was decreased from 12 to 3 h.[5] Since the benzoin condensation results in step-growth polymerization, reduction of the polymerization time will reduce the molecular weight. As is generally known, a step-growth polymerization takes place in statistical steps. First, the monomers will react to form dimers, and only after many dimers have formed, the dimers will start to react with monomers or dimers to form trimers or tetramers. This means that the molecular weight will be built up very slowly.[6,7]

To enable longer polymerization times, other solvents were tried, instead of the original methanol. First, nonalcoholic polar solvents and later sterically hindered alcohols were tried in order to avoid the side reaction.

Scheme 1. Synthetic Route to Poly(thiophene-2,5-diyl-1,2-dimethoxyvinylene)



Polar Nonalcoholic Solvents. The choice of polar solvents was inspired by the fact that the polyacyloin is insoluble in common organic solvents (water, methanol, chloroform, ethers, hydrocarbons) and precipitation causes polymerization to stop at low molecular weights. The insolubility is probably caused by intramolecular hydrogen bonds, and breakdown of these bonds makes the polyacyloin soluble in polar solvents.

The solvent choice is restricted because neither aldehydic nor ketonic solvents can be used as they react with potassium cyanide. Pyridine was selected out of a list given by Reichardt.[8]

Other reaction conditions were not changed, and after 18 h, a viscous black solution was formed without a precipitate. Evaporation of the reaction mixture yielded a black solid which dissolved in methanol and water and precipitated in chloroform and diethyl ether. It was obvious that no polyacyloin but instead a charged molecule was formed. The product was purified by dialysis in deionized water for 4 days (Visking membrane, molecular weight cutoff 3500 Da).

Photoacoustic spectroscopy infrared (PAS-IR) and ^1H NMR showed that a copolymer was formed with the acyloin as one monomeric unit. For the other unknown unit, the IR spectrum showed signals for pyridine, thiophene, alcohols, and the cyanide ion. In the NMR spectrum aliphatic and aromatic signals occurred. From these data it was concluded that probably the structure shown in Figure 1 was formed.

The copolymer was formed through substitution of the cyano group by pyridine. Evidence was found by performing the reaction with pyridine as the solvent but without KCN. No reaction occurred, and after 24 h the unreacted aldehyde was recovered.

Since the use of polar, nonalcoholic solvents did not yield the required results, another solution had to be found.

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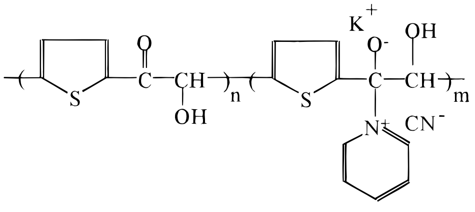


Figure 1. Possible structure of the copolymer formed by using pyridine as the solvent.

Table 1. Influence of Solvent and Reaction Time on the Molecular Weight of Poly(2,5-thienylene-1-oxo-2-hydroxyethylene)

	methanol (3 h)	*tert*-butyl alcohol (5 h)	cyclohexanol (6 h)	cyclohexanol (22 h)
M_w	427 000	373 000	1 270 000	956 000
M_n	15 000	12 000	99 000	60 000
pd	28.2	31.0	12.7	15.9

Alcohols. The influence of alcohols, less nucleophilic than methanol, on reaction time and molecular weight was investigated. We tested 1,3-dichloro-2-propanol, *tert*-butyl alcohol, and cyclohexanol. 1,3-Dichloro-2-propanol gave only the side reaction, and no polyacyloin was formed. The reaction with *tert*-butyl alcohol yielded after 5 h only polyacyloin, but after 23 h of reaction the dimethyl ester was found to be the major product. With cyclohexanol as the solvent, the side reaction did not occur even after 22 h and the yield (43%) of polyacyloin was the same as in methanol.

The molecular weights of the polymers were determined by gel permeation chromatography using a MIXED B (10 μm) column (Polymer Laboratories). The calibration was based on narrow polystyrene standards ranging from 6 850 000 to 1320. The results shown in Table 1 can only be used for relative comparison, the true molecular weight of the rigid polymer is probably lower. Earlier GPC experiments on PTV precursors had proved that the molecular weight is overestimated by a factor of 3 unless a calibration is used based on the precursor itself.[9] Nevertheless, the data clearly show that a 3-fold increase of the average molecular weight is possible by doubling the reaction time. It is of interest to note that the molecular weight decreases over long reaction periods (see cyclohexanol); this may be caused by degradation of the polymer chain.

Poly(2,5-thienylene-1-oxo-2-hydroxyethylene), synthesized in methanol (M_w = 427 000 Da), was oxygen alkylated to the corresponding poly(thiophene-2,5-diyl-1,2-dimethoxyvinylene) (MOPTV). GPC measurements of this polymer gave a surprisingly low molecular weight, M_w = 2500 Da. It seemed that during the oxygen alkylation a drastic decrease in the molecular weight had taken place. A thorough investigation of the oxygen alkylation was therefore necessary.

Oxygen Alkylation. The oxygen alkylation normally takes 15 h. As observed earlier the molecular weight decreases with increased reaction times. Therefore, the alkylation was monitored with respect to time. Samples taken at regular intervals were analyzed by GPC (chloroform as eluent) and UV spectroscopy. The data (Table 2) show that after 30 min degradation has already occurred and that 15 h of reaction does not lead to significantly higher molecular weights.

A GPC sample taken after 6 h of alkylation was exposed to air and sunlight, upon which it showed discoloration from orange to yellow, and a decrease in molecular weight from 2800 to 900 Da. Thus, we performed henceforth the workup of the alkylation reaction under nitrogen protection. Then, GPC analysis of the product gave M_w = 700 000, M_n = 11 000 and pd = 63, consistent with the polyacyloin results.

Table 2. UV and GPC Results While Monitoring the Oxygen Alkylation in Time

reaction time (h)	UV λ_{max} (nm)	GPC M_w (Da)
0.5	399	2200
1	397	2300
1.5	397	2600
2	394	2400
3	397	2500
4	394	2300
5	397	2500
6	397	2800
15	397	2500

Keeping the polymer in a stoppered but not darkened vessel resulted in a decrease of M_w to about 6000 in 5 weeks. It seemed that for the degradation both light and air are required, and hence stability studies were performed.

Photooxidation

Stability studies of poly(3,4-dibutoxy-2,5-thienylenevinylene) have been described by Blohm et al.[10,11] These authors suggested that the polymer was sensitive to ozone in the air and to photooxidation. They rationalize that butoxy substituents enhance the electron density of the thiophene ring and so render the compound more unstable to environmental conditions. To find out what caused the degradation of MOPTV, we performed the following experiments.

To start with, incomplete alkylation had to be ruled out. Incomplete alkylation will leave enolates in the reaction mixture, which are very reactive toward oxygen.[12] Because BuLi and *t*-BuOK are used, remaining enolates will carry Li and/or K counterions. Atomic absorption spectroscopy showed negligible amounts of these metals (Li 0.14% w/w; K 0.57% w/w) after alkylation, proving that enolates are not responsible for the polymer degradation.

Next, as suggested by Blohm et al.,[10,11] we tested the reaction of the vinylene group with ozone, a (possible) component of air. Pure MOPTV films were cast from a CH_2Cl_2 solution onto a glass substrate and immediately brought into a glass reactor tube of 30 cm length. With the help of a Litha ozonizer, air was enriched to an O_3 concentration of 5×10^{-3} g/L (normal O_3 concentration 5×10^{-9} g/L) and pumped over the films at a flow rate of 300 mL/min. Three series of experiments were performed:

Series i: the films were under continuous illumination by a 60 W lamp.

Series ii: the films were kept in total darkness.

Series iii: before the reactor tube a tube containing 150 g of HIPS (HIPS is an acryonym for high-impact polystyrene, a polystyrene containing 14% w/w butadiene) was placed acting as an O_3 scavenger. Furthermore, instead of a pure MOPTV film, a blend film, made of a mixture of 7% w/w MOPTV and 93% w/w HIPS, was exposed to O_3-enriched air under continuous illumination by a 60 W lamp.

In another three series of experiments (series iv−vi) in the previous experiments were repeated, but now exposing the films to normal laboratory air and for series iv and vi under illumination of a normal day/night rhythm. In all cases UV spectra were recorded at

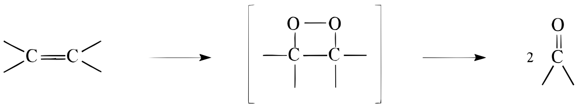
Table 3. Half-Life Times, $\tau_{1/2}$, of Extinction at $\lambda = 450$ nm in MOPTV Films under Oxidative Conditions (See Text)

series	condition	$\tau_{1/2}$
i	O_3; illumination	3 h
ii	O_3; dark	3.2 h
iii	"O_3 removed"; illumination	8 h
iv	air; illumination	40 days
v	air; dark	460 days
vi	"O_3 removed"; illumination	60 days

regular intervals. We found that the longest wavelength absorption started at $\lambda_{max} = 450$ nm and shifted via $\lambda_{max} = 310$ nm to $\lambda_{max} = 270$ nm over 6 h (series i–iii) or over 50 days (series iv–vi). This shows that the polymer chain breaks at random places, producing short chains and widening the molecular weight distribution toward the low molecular weights, as was also observed by GPC. Such a behavior is typical for oxidations. Furthermore, the extinction at $\lambda = 450$ nm decreased in all cases almost exponentially with time. The half-life times, $\tau_{1/2}$ (i.e., the time in which the extinction decreased to 50% of the original value), are given in Table 3.

The data show that removal of O_3 by HIPS increases $\tau_{1/2}$ of the films by about the same factor: $\tau_{1/2}$ (series iii)/$\tau_{1/2}$ (series i) = 2.7 and $\tau_{1/2}$ (series vi)/$\tau_{1/2}$ (series iv) = 1.5. In contrast, exclusion of light has little influence on the O_3-promoted but a large influence on the air-promoted breakdown: $\tau_{1/2}$ (series ii)/$\tau_{1/2}$ (series i) = 1.1 and $\tau_{1/2}$ (series v)/$\tau_{1/2}$ (series iv) = 12. This proves that O_3 is not the major contributor to the air-promoted breakdown and strongly suggests molecular oxygen as the major oxidant. Corroborating evidence was found in a significant stabilization of MOPTV films when an industrial antioxidant (Kerobit) was added to the MOPTV/HIPS blend.

Normally, double bonds do not react with molecular oxygen, but exceptions are known, particularly when singlet oxygen is involved. For example, Gollnick[13] and independently Foote[14,15] observed allylic hydroperoxides as the major products from singlet oxygen reaction with olefins. Later, Kearns et al.[16] found experimental evidence for the presence of dioxetane and perepoxide intermediates in singlet oxygen reactions with olefins. Olefins without allylic hydrogens always gave carbonyl fragments, which led to the following mechanism:[17]



The mechanism was supported by Kopecky,[18] who observed that dioxetanes of methyl-substituted ethylenes thermally decompose to carbonyl derivatives. Furthermore, carbonyl cleavage was promoted by the conjugation of the double bonds with phenyl groups or other double bonds as well as by substitution with electron-donating groups.[16] This information leaves little doubt about the degradation mechanism of MOPTV. The polymer contains no allylic hydrogen atoms and is conjugated and substituted with electron-donating groups. All conditions are fulfilled for the dioxetane mechanism to occur. More evidence was found in thermogravimetric Fourier transform infrared measurements. The signal at E in the thermogram (see Figure 2) was characterized as acetic acid by infrared spectroscopy. This result is in agreement with those of the photosensitized oxidation of 1,2-dimethoxystilbene performed in acetone solution by Bartlett.[19] 1,2-dimethoxystilbene was converted in a 96% yield to methyl benzoate via the dioxetane mechanism. Figure 3 depicts the mechanism we propose for the photochemical oxidation of MOPTV. While this work was in progress, Scurlock et al.[20] suggested the same mechanism for the photodegradation of poly(2,5-bis(5,6-dihydrocholestan-3-oxy)-1,4-phenylenevinylene). Hence, it may be concluded that this degradation mechanism applies to all poly(arylenevinylenes).

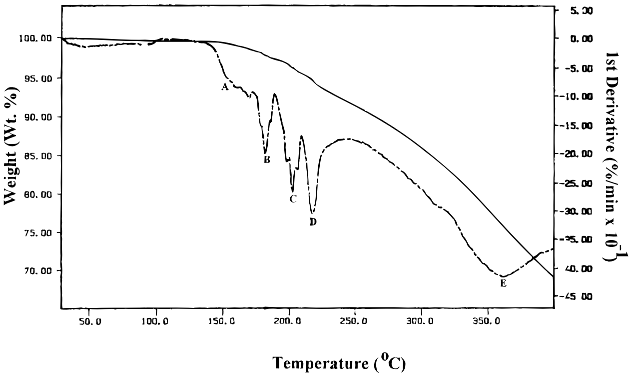


Figure 2. Thermogravimetric analysis of poly(thiophene-2,5-diyl-1,2-dimethoxyvinylene): (—•—) first derivative (%/min × 10^{-1}); (—) wt %.

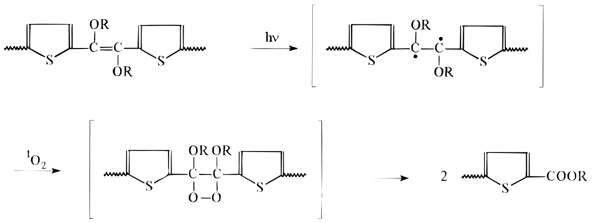


Figure 3. Degradation mechanism proposed for MOPTV and other poly(arylenevinylenes).

Material Properties

MOPTV was doped with iodine from the gas phase to a conductivity of 0.4 S/cm.

The thermogravimetric analysis showed (Figure 2) that MOPTV starts to decrease in weight from 150 °C (point A) onward. Infrared spectra taken of the outgoing gases at the maxima (B, C, D of Figure 2) reveal signals at 3000 and 1050 cm^{-1}. They are typical for methanol and point out that the two methoxy groups split off. We recall that the infrared spectrum of the gases evolved at 360 °C (E in Figure 2) shows a major signal at 1740 cm^{-1}. We attribute this to acetic acid, formed in the split off of carboxylic groups, which themselves were formed earlier in a reaction of MOPTV with molecular oxygen.

Differential scanning calorimetry performed on MOPTV showed (Figure 4) a glass–rubber transition T_g = 91 °C with a change in heat capacity $\Delta C_p = 0.316$ J g^1 °C^{-1}.

Experimental Section

Poly(2,5-thienylene-1-oxo-2-hydroxyethylene). To a mixture of 5.9 g of 2,5-thiophenedicarboxaldehyde (0.04 mol) and 125 mL of alcohol/water (1:1) was added dropwise a mixture of 3.33 g of KCN (0.05 mol) and 30 mL of alcohol/water (1:1). The reaction mixture turned dark red. After 30 min a precipitate was formed, and the mixture was stirred for an additional 2.5 h or longer depending on the alcohol used (MeOH 2.5 h; *t*-BuOH 4.5 h; cyclohexanol 5.5 h or longer). The precipitate was filtered off and washed with 600 mL of water

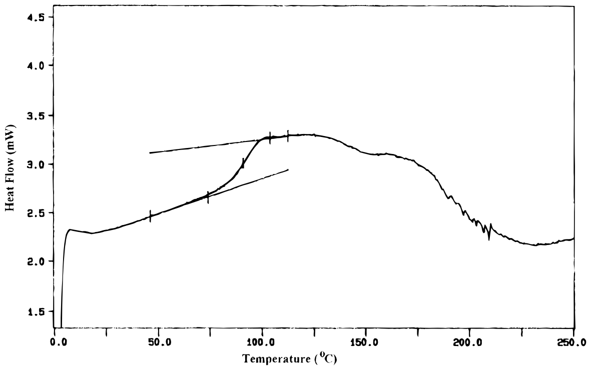


Figure 4. Differential scanning calorimetric analysis of MOPTV.

and 100 mL of methanol. Purification by a Soxhlet extraction with chloroform yielded 2.32 g (40.5%), mp >310 °C. IR (cm^{-1}) 3300 (O−H stretch), 3107 (aromatic C−H stretch), 1666 (conjugated ketone), 1518 (ring-breathing thiophene), 1189 (*tert*-alcohol C−O stretch), 818 and 744 (out-of-plane C−H bending). ^{1}H NMR (δ, ppm) 7.9 (thiophene), 3.6 (alcohol), 2.6 (aliphatic proton). ^{13}C NMR (δ, ppm) 180 (ketone), 144 (*quat*-C-atom thiophene), 138 (*tert*-C-atom thiophene), 76 (aliphatic C-atom).

Poly(thiophene-2,5-diyl-1,2-dimethoxyvinylene). The synthesis was performed in a three-step one-pot reaction. First, a Schlösser base[21] was made in order to yield a polydianion in step 2. Thereafter, the oxygen alkylation took place.

It is necessary to work under an inert, oxygen-free atmosphere.

Schlösser Base. *t*-BuOK (1.2 g, 10.7 mmol) and dry THF (160 mL) where brought into a three-necked flask under a nitrogen atmosphere. The solution was cooled to −78 °C, and 4.28 mL of *n*-BuLi (2.5 M hexane solution, 10.7 mmol) was gently added dropwise. The solution was stirred at −78 °C for an additional 15 min and immediately used in the next step.

Polydianion. To the Schlösser base, a solution of 0.3 g of poly(2,5-thienylene-1-oxo-2-hydroxyethylene) in 32 mL of dimethyl sulfoxide (DMSO) was added dropwise. The reaction mixture turned black upon this addition. The solution, now containing the dianion of the acyloin, was slowly heated to room temperature before the alkyl reagents were added.

Oxygen Alkylation. Freshly distilled dimethyl sulfate (2.7 mL, 29 mmol) was added to the dianion solution. The reaction mixture was stirred for 2 h at room temperature, during which time the solution became viscous. This oil still contained DMSO, which was removed by adding the oil dropwise to water while stirring vigorously under nitrogen protection. The polymer precipitated and was filtered off. Further purification was carried out by dissolving the polymer in chloroform and subsequent precipitation in vigorously stirred hexane under N_2 atmosphere. The impurities dissolved in hexane. Yield 0.15 g (42%), mp 154 °C. IR (cm^{-1}) 3100 (=CH stretch), 2960 (saturated C−H stretch), 2830 (CH_3 group in OCH_3), 1718 (conjugated C=C stretch), 1510 (C=C thiophene, conjugated), 1447 (aromatic C−H bending), 1259 (C−O−C stretch ether), 751 (thiophene). ^{1}H NMR (δ, ppm) 7−8 (thiophene, broad 2H), 3.8 (methoxy, broad, 6H).

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