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Synthesis and Polymerization of Substituted Aryl Vinyl Sulfoxides. On-Line Monitoring and Kinetics of the Thermal Degradation of Polymeric Sulfoxides into *trans*-Polyacetylene

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ABSTRACT: The substituted aryl vinyl sulfoxides *p*-[$RC_6H_4S(O)CH{=}CH_2$] (**8a–c**, R = F, Cl, OMe) were prepared and polymerized in the presence of (3-methyl-1,1-diphenylpentyl)lithium (MDPPLi, **1**) as anionic initiator to give the corresponding poly(aryl vinyl sulfoxides) **9a–c**. Upon thermolysis of compounds **9** between 70 and 120 °C, the arenesulfenic acids (**10**) were eliminated *via* an E_i mechanism generating *all-trans*-polyacetylene (PA, **11**). The formation of *all-trans*-PA was monitored on-line by means of near-infrared-excited Fourier-transform (FT)-Raman spectroscopy. The kinetics of the reaction were found to be first-order at conversions above approximately 10%. On the basis of the rate constants determined for the thermolysis of **9a–c** at 70, 80, 90, 100, and 120 °C, the relative reactivities of **9a–c**, and thus the influence of the substituents R on the rate of the PA formation, could be quantitatively estimated, and the following ratios were found: **9a** (R = F):**9b** (R = Cl):**9c** (R = OMe) = 1.0 ± 0.1:2.2 ± 0.3:0.8 ± 0.1.

Introduction

Polyacetylene (PA) is one of the most interesting electroactive polymers due to its high conductivity[1] and large third-order nonlinear optical activity.[2] Different strategies have been developed to synthesize PA, such as the Ziegler–Natta[3] and the Luttinger–Green[4] polymerization of acetylene gas. However, due to serious drawbacks associated with these methods, *e.g.* oligomerization and insolubility, precursor routes have been introduced by Feast[5] and Hogen-Esch.[6] The thermal elimination of benzenesulfenic acid from poly(phenyl vinyl sulfoxide), PPVS,[6,7] is a novel synthetic pathway to PA. In this work we present the synthesis of *para*-substituted aryl vinyl sulfoxides and the anionic polymerization of these new monomers into substituted PPVS derivatives. Further, the formation of PA by thermal degradation of the various polymeric sulfoxides was monitored on-line by means of FT-Raman spectroscopy.

Results and Discussion

Poly(phenyl vinyl sulfoxide) (PPVS, **3**) is easily synthesized by the anionic polymerization of phenyl vinyl sulfoxide (PVS, **2**) at −78 °C in tetrahydrofuran (THF; see Scheme 1). Excellent initiators for the polymerization of **2** are delocalized carbanions such as (3-methyl-1,1-diphenylpentyl)lithium (MDPPLi, **1**). Molecular weights up to 22 500, *i.e.* 150 repeating units, are obtained using **1** as catalyst. PPVS (**3**) is air-stable and soluble in common organic solvents. Notably, the polymerization also proceeds using methyllithium or (triphenylmethyl)lithium as initiators.

The substituted monomers are prepared according to a procedure described by Paquette *et al.*[8] Commercially available substituted thiophenols **4a** (R = F), **4b** (R = Cl), and **4c** (R = OMe) were transformed into their sodium salts by treatment with sodium ethoxide (see Scheme 2). The reaction mixture was slowly added to a solution of 1,2-dibromoethane (**5**) in ethanol while the reaction temperature was maintained at 25–30 °C by cooling with an ice bath. After the mixture was stirred under nitrogen for 30 min, compounds **6a–c** were formed and subsequently treated with sodium ethoxide for another 8–12 h. Then, the resulting mixture was stirred under reflux for 5–8 h, and the progress of the reaction was monitored by TLC. After aqueous workup, the isolated vinyl sulfides **7a–c** were purified by vacuum distillation. Oxidation of the substituted aryl vinyl sulfoxides **7a–c** was accomplished by treatment with hydrogen peroxide in glacial acetic acid in the presence of catalytic amounts of sodium tungstate.[9] The reaction temperature was maintained between 20 and 25 °C by cooling with an ice bath. After aqueous workup, the products were purified by distillation to give **8a–c** in overall yields of 43, 55, and 49%, respectively.

Due to the reduced electron-donating effect of the sulfur atom in the sulfoxides **8a–c** compared to **7a–c**, the ^{1}H-NMR resonances of the proton attached to C-1 are shifted toward lower fields and could be detected at approximately $\delta = 6.5–6.6$ ppm. The proton *trans* to the methine hydrogen is located in the anisotropy cone of the sulfoxide group and shifted to $\delta = 5.9–6.1$ ppm. Coupling constants of $J > 15$ Hz are found for the *trans* arrangement and $J = 10$ Hz for the *cis* configuration. A strong band at $\nu = 1050$ cm^{-1} in the IR spectra is typical of the sulfoxide structure.

The polymerization of **8a–c** was carried out at −78 °C in THF using MDPPLi (**1**) or methyllithium as initiator. The solvent (THF) was first distilled from copper(I) chloride to remove traces of peroxides and was then further purified by heating over sodium metal under nitrogen for 24 h. Monomers **8a–c** were distilled three times from calcium hydride to remove traces of acid. A certain amount of initiator was injected, the mixture was cooled to −78 °C, and the monomer was subsequently added. The greenish-yellow color of the solution indicated the presence of the "living" α-lithio sulfinyl carbanion. After 30 min, the reaction was quenched by adding an excess of deoxygenated methanol. PPVS (**3**) and its derivatives (**9a–c**) were isolated as white powders by precipitation with diethyl ether.

The ^{1}H-NMR spectra of **9a–c** show signals at $\delta = 2$ ppm which are due to the methylene groups in the polyethylene chain, whereas the CH protons resonate around $\delta = 3.3$ ppm. For the 1,4-disubstituted aryl system an AA′BB′-coupling pattern was found between

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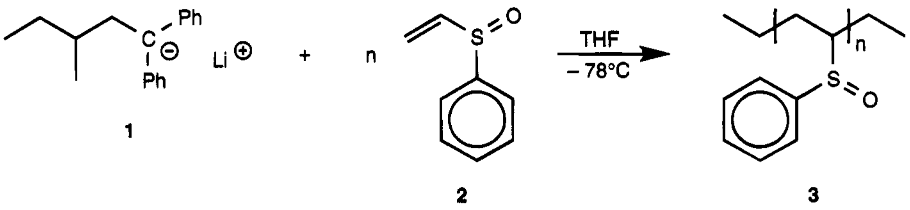
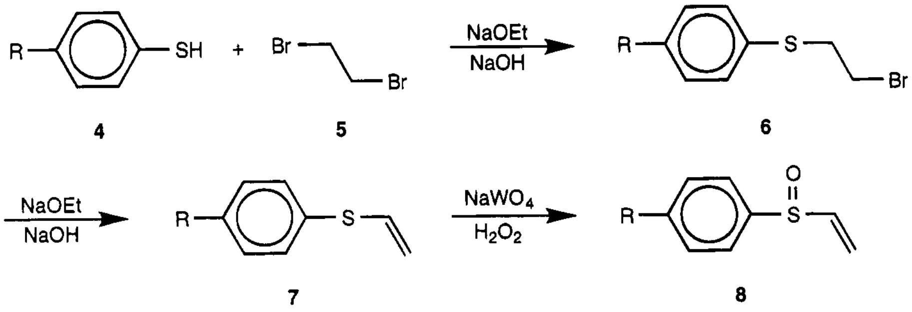
Scheme 1

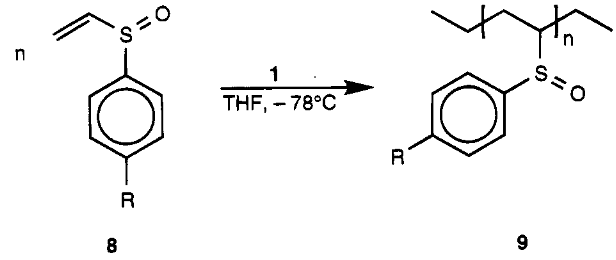


Scheme 2

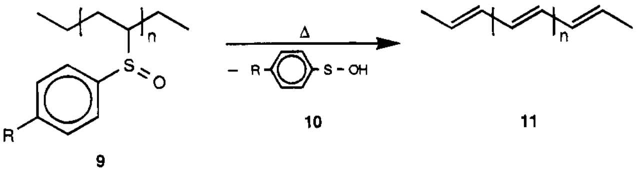


4, 6-10	R
a	F
b	Cl
c	OMe

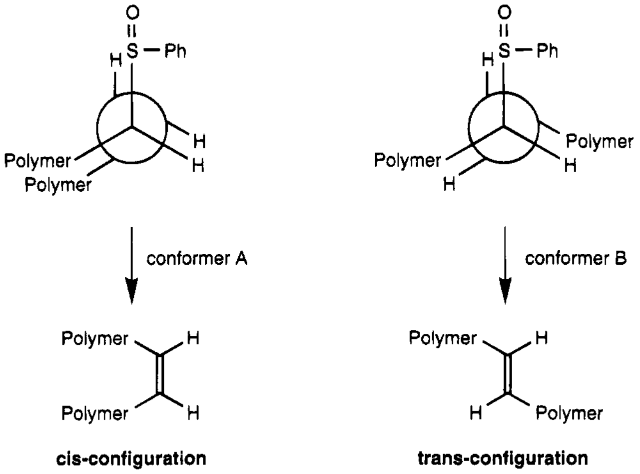
Scheme 3



Scheme 4



Scheme 5



$\delta = 6.7$ and 7.7 ppm. The infrared spectra show the characteristic sulfoxide bands at $\nu = 1042-1046\ \mathrm{cm}^{-1}$ and the significant absorption bands for the *para* substituent around $\nu = 1080-1095\ \mathrm{cm}^{-1}$. Molecular weight ($M_w$) determinations using polystyrene (Ultrastyragel) as a standard gave the following values: **9a**, 10 435; **9b**, 12 018; **9c**, 10 358. The differential scanning calorimetry (DSC) analyses of compounds **9a**–**c** in the range 10–410 °C at a heating rate of 5 °C/min revealed three exothermic peaks ranging from 75 to 110, 110 to 140, and 155 to 250 °C. The peaks observed during the decomposition of **9a**–**c** support the findings of Mathis *et al.*[7]

Thermal treatment of the poly(aryl vinyl sulfoxides) **9a**–**c** at temperatures above 50 °C resulted in the elimination of the corresponding sulfenic acids (**10**) to give *all-trans*-PA (**11**) (see Scheme 4). The free sulfenic acids, however, are unstable and are believed to decompose by dehydration, presumably *via* a cyclic intermediate,[10a] into thiosulfinates [RS(O)SR], which in turn readily disproportionate to give a mixture of thiosulfonates [RSO_2SR] and disulfides [RSSR].[10b–d] Due to the rapid and irreversible decomposition of the sulfenic acids (**10**) under the reaction conditions, a significant re-formation of the starting poly(aryl vinyl sulfoxides) (**9**) from the products may be excluded. Moreover, a major buildup of volatile, monomeric reaction products, which may affect the elimination, was prevented by applying a constant flow of nitrogen over the reaction mixture.

The mechanism of the elimination of sulfenic acids from sulfoxides is supposed to be of E_i type involving a five-membered, cyclic transition state similar to that of the well-known Cope reaction of amine oxides.[10e–g] Similarly, the related elimination reaction from a discrete sulfoxide group proceeds with *syn* stereochemistry.[10h–k] In the case of acyclic sulfoxide, the regioselectivity of the double bond formation during the pyrolysis is determined by the most acidic β-hydrogen.

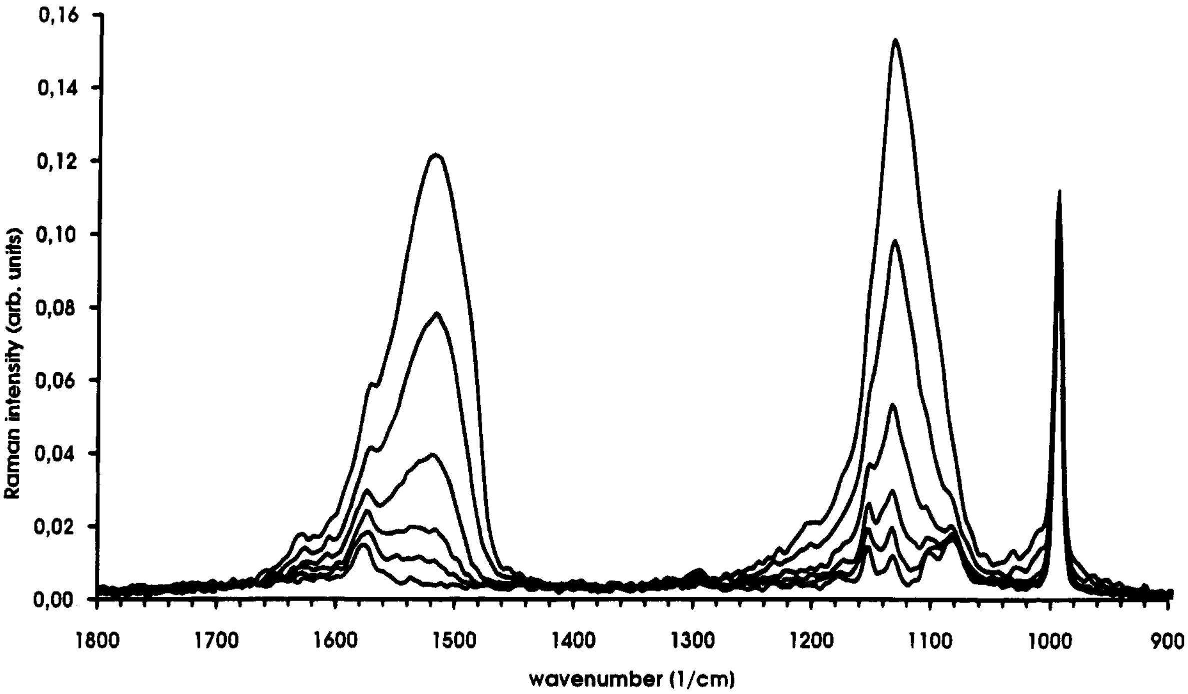


Figure 1. FT-Raman spectra recorded during the thermolysis of poly(*p*-chlorophenyl vinyl sulfoxide) (**9b**) at 90 °C after 1, 3, 4, 5, 6, and 7 min.

Scheme 5 shows the Newman projections of the two conformers A and B which, upon elimination of sulfenic acid, yield *cis*- and *trans*-PA, respectively. In both conformers, the α-hydrogen atom adopts a synclinal orientation with respect to the sulfoxide moiety. Conformer A is less favorable than conformer B due to strong steric interactions of the eclipsed polymer chains. Therefore, even at elevated temperatures, sulfenic acid elimination selectively proceeds *via* conformer B, yielding *all-trans*-PA, which is experimentally confirmed by the absence of Raman bands due to *cis*-PA at around 1250 and 1540 cm^{-1}.[11a] These results are in keeping with findings by Trost and Salzmann.[10j,k]

The thermally induced isomerization of *cis*-PA into the more stable *trans*-PA requires temperatures well above 120 °C to proceed at significant reaction rates, as shown by Heeger *et al.*[11b] Hence, under the reaction conditions of the present work, the initially unselective formation of a mixture of *trans*-PA and *cis*-PA followed by a rapid thermal conversion of the latter into *trans*-PA can be excluded.

On-Line Monitoring of the Polyacetylene Formation by Means of FT-Raman Spectroscopy

In order to examine the influence of the *para* substituents F, Cl, and OMe in the poly(aryl vinyl sulfoxides) (**9**) on the rate of the sulfenic acid elimination according to Scheme 4, the kinetics of the thermal degradation of **9a**–**c** into *all-trans*-PA (**11**) were investigated between 70 and 120 °C. Particular attention must be paid to the experimental requirements associated with the monitoring of the PA formation in the course of the reaction. Especially at high reaction rates with half-lives in the range of only a few minutes, the use of a fast spectroscopic technique suitable for *in-situ* measurements rather than a discontinuous analytical method is imperative. For the present study, near-infrared-excited Fourier-transform (FT)-Raman spectroscopy was chosen as the analytical tool:[12] polyenes show large Raman scattering cross-sections, a prerequisite for obtaining intense spectra. Moreover, the use of near-infrared excitation (1064 nm) provided by a neodymium yttrium aluminum garnet (Nd^{3+}:YAG) laser ensures that the spectra are free from background fluorescence[12a,c,e] and thus amenable to quantitative evaluation. Due to the very intense Raman scattering of PA, the power and the focusing of the incident laser beam could be significantly reduced and sample degradation thus avoided.[12a–d,f] Despite the loss of intensity caused thereby, satisfactory signal-to-noise ratios were obtained.

Considerable theoretical effort has been devoted to the vibrational analysis of *cis*- and *trans*-PA and to the interpretation of the infrared and Raman spectra of this class of compounds.[12a,13a–f] A factor group analysis of *all-trans*-PA (**11**) on the basis of a repeating unit of C_{2h} symmetry (*i.e.* alternating carbon–carbon distances) revealed that there are four Raman- (A_g) and two IR-active (B_u) vibrational modes to be expected.[13a] The two most prominent Raman bands of *all-trans*-PA (**11**) appear around 1130 cm^{-1} (ν_1) and 1530 cm^{-1} (ν_2) and are associated with the carbon–carbon single bond stretch coupled to C–H in-plane bending modes and the carbon–carbon double bond stretch, respectively.[12a] It must be noted that the actual position of the ν_2 frequency for a given laser wavelength is a function of the number of conjugated C=C bonds within the backbone.[13a] This gives rise to a particular ν_2 band profile, the shape of which depends on the distribution of the various polyene sequence lengths in the sample. In the kinetic experiments described in this work, the gradual buildup of the polyene system from fully saturated precursors was monitored. Accordingly, a certain range of conjugation lengths was expected to be present in the samples, thus giving rise to some band broadening in the Raman spectra.

Figure 1 shows a series of Raman spectra recorded on-line during the thermolysis of poly(*p*-chlorophenyl vinyl sulfoxide) (**9b**) at 90 °C. The formation of PA can easily be monitored by the growing bands in the regions around 1130 and 1530 cm^{-1}. The signal at 995 cm^{-1} is due to the symmetrical S–O stretch of sodium sulfate,

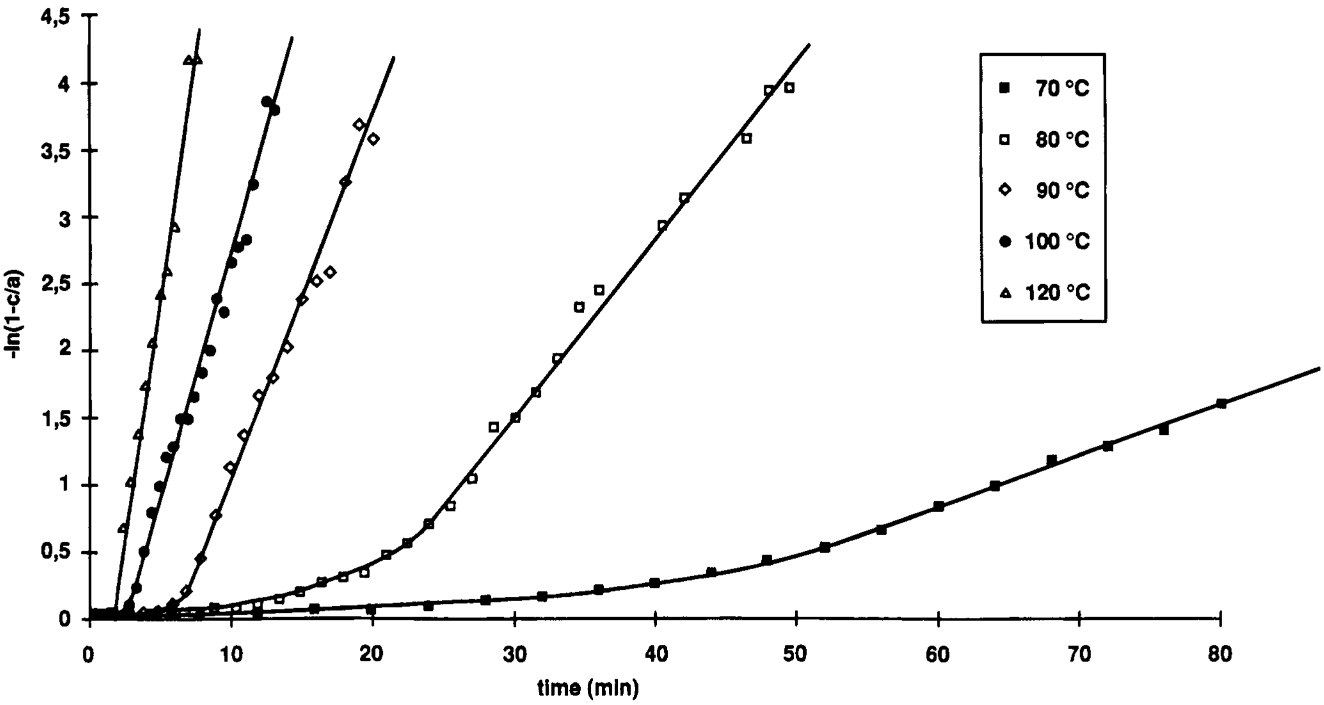


Figure 2. First-order plots for the thermal degradation of poly(*p*-chlorophenyl vinyl sulfoxide) (**9b**) into PA at various temperatures.

which was used as a matrix in the sample (*vide infra*). The spectra are dominated by the signals of *all-trans*-PA (**11**), whereas the contributions of the starting sulfoxides (**9**) and the side products, *i.e.* sulfenic acids (**10**) or their decomposition products, are small and remain practically constant throughout the reaction.

Quantitative analysis using Raman spectroscopy has attracted increasing attention only recently, especially in the field of polymer science.[12g,14] Experiments conducted hitherto suggest that both spectrometer stability and sample preparation are of paramount importance for obtaining reliable and reproducible data. In the case of solids, inhomogeneities of the sample surface may lead to erroneous results. For this reason, various preparation techniques, *e.g.* rapid rotation of the sample pellet,[14j] have been investigated in the past, and the spectroscopic results were examined with respect to reproducibility and applicability to quantitative analysis. In our studies, we used stationary samples; however, due to the weak focusing of the laser beam, a large surface area was irradiated and contributed to the recorded Raman intensity, thus averaging inhomogeneities. Preliminary experiments revealed that the Raman spectroscopic monitoring of the PA formation gave unsatisfactory results when the starting materials **9** were used in their pure forms. This observation may be explained in terms of the considerable changes of the sample surface (especially of the particle size) occurring in the course of the reaction. In order to minimize such effects, the starting sulfoxides (**9**) were incorporated in a matrix of excess (1/4, *m*/*m*) sodium sulfate, which, due to its inertness, effectively stabilizes the surface properties during the reaction. The Raman band due to the sodium sulfate matrix (ν = 995 cm^{-1}; see Figure 1) is expected to remain unchanged throughout the reaction and was therefore used as an internal reference.[14i,k] Accordingly, the spectra recorded in each kinetic experiment were normalized to the intensity of the sulfate signal, thus compensating for effects caused by any changes in either sample positioning or spectrometer stability.

For the quantitative evaluation of the sequence of Raman spectra recorded during the thermolysis of **9a**–**c** (see Figure 1), the integral of the ν_2 PA band centered around 1530 cm^{-1} (integration limits: 1430–1680 cm^{-1}) was used as a direct measure of the PA content in the sample. As the conversion of the reaction approaches 100%, the ν_2 band integral reaches a maximum, the value of which, even after continued thermal treatment of the sample, remains constant within the experimental error (approximately 7%). The E$_i$ mechanism proposed for the reaction (see Scheme 5) suggests a formal first-order kinetic behavior for the formation of PA. Equation 1 describes the relevant rate law in logarithmic form

$$kt = -\ln[1 - c/a] \qquad (1)$$

where k designates the rate constant, c the ν_2 band integral, *i.e.* the "concentration" of PA, at the reaction time t, and a represents the maximum ν_2 band integral observed at nearly quantitative conversion.

According to eq 1 the kinetics are experimentally described by the ratio c/a, and it is therefore not necessary to determine the absolute concentration of PA in the sample. Figure 2 shows the plots $-\ln(1 - c/a)$ *vs* t for the thermal degradation of poly(*p*-chlorophenyl vinyl sulfoxide) (**9b**) at 70, 80, 90, 100, and 120 °C. Compounds **9a,c** exhibit analogous behavior. The graphs clearly illustrate that at conversions above approximately 10%, the experimental data may be fitted to a straight line, confirming that the reaction can formally be described by a first-order kinetic law. The rate constant k, as defined by eq 1, may be evaluated from the slope of the curves in the linear region. At low conversions, however, the reaction does not obey first-order kinetics, and the rate constants gradually increase until they reach a constant value. The duration of this "induction period" crucially depends on the reaction temperature and, for poly(*p*-chlorophenyl vinyl sulfoxide) (**9b**), ranges from 2 min at 120 °C to approximately 40 min at 70 °C (see Figure 2). This observation may be explained in terms of a considerable decrease of the

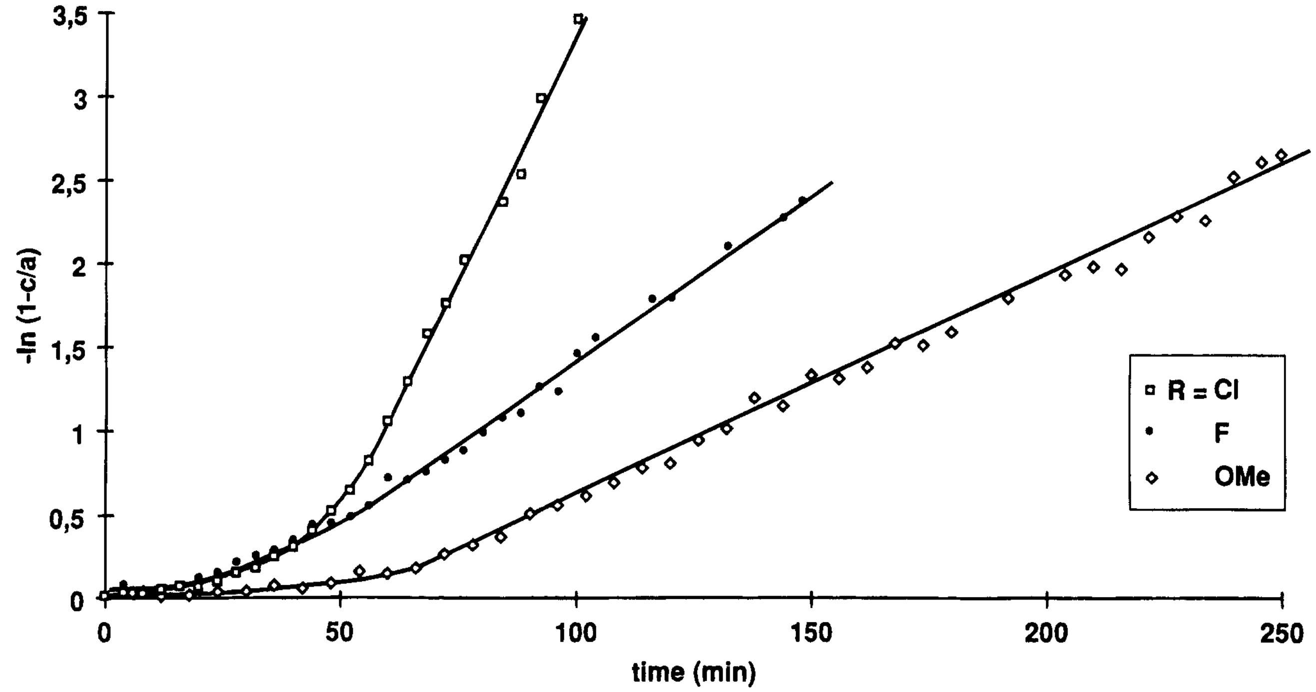


Figure 3. First-order plots for the thermal degradation of the poly(aryl vinyl sulfoxides) **9a–c** at 70 °C.

Table 1. First-Order Rate Constants *k* (min^{-1}) for the Thermolysis of the Poly(aryl vinyl sulfoxides) 9a–c

temp (°C)	9a	9b	9c
70	0.020	0.051	0.014
80	0.060	0.132	0.049
90	0.133	0.292	0.101
100	0.180	0.360	0.172
120	0.333	0.682	0.280

activation barrier associated with the formation of an additional double bond in conjugation to a short polyene system. In the case of higher conjugation lengths, the additional resonance stabilization due to a newly formed double bond becomes less important.

Table 1 compiles the rate constants *k* for the thermolysis of **9a–c** at various temperatures. The data allow a quantitative treatment of the kinetic influence of the substituent R in the poly(aryl vinyl sulfoxides) **9** on the elimination of the respective sulfenic acid (see Scheme 4). On the basis of the values collected in Table 1, the reactivities of **9a–c** may be compared in terms of their first-order rate constants. The following ratios were calculated: **9a** (R = F):**9b** (R = Cl):**9c** (R = OMe) = 1.0 ± 0.1:2.2 ± 0.3:0.8 ± 0.1. These results, which are illustrated in Figure 3, fully corroborate preliminary qualitative experiments on sulfoxide films, according to which the chloro-substituted precursor reacts considerably faster than the methoxy-substituted analogue.

Experimental Section

Tetrahydrofuran (THF) was purified by distillation from copper(I) chloride and subsequent heating under reflux over sodium wire for 24 h followed by distillation under nitrogen. Other reagents and materials were obtained from commercial suppliers and were used without further purification. All reactions were carried out under inert gas, and conversions were checked by TLC. ^{1}H and ^{13}C NMR: Bruker AC 400; multiplicities were determined with the DEPT pulse sequence. MS: Varian MAT 311A. IR: Bruker IFS 28 and Perkin-Elmer lambda 5. TLC: Macherey-Nagel Polygram SIL G/UV$_{254}$. The molecular weight (M_w) of the polymers was determined by gel permeation chromatography (GPC) using polystyrene as a standard. Raman investigations were performed on a Bruker IFS 66 FT-IR spectrometer equipped with an FRA 106 Raman module and a liquid nitrogen cooled germanium detector. Laser excitation was provided by a diode-pumped Nd^{3+}:YAG near-infrared laser (λ = 1064 nm) operated at a power of 35 mW. Data handling and spectral manipulations were carried out using the Bruker software package OPUS. Before and after each experiment, the spectrometer stability was checked by measuring a standard sulfur sample. In order to avoid aerial oxidation of the polyacetylene,[12d] and to remove volatile side products, the sample compartment was constantly purged with nitrogen. The samples were prepared as follows: the particular poly(aryl vinyl sulfoxide) (**9a–c**) was thoroughly ground with anhydrous sodium sulfate in the ratio of 1/4 (*m*/*m*), and the mixture was placed into the sample cell ("powder cup"). The cell consisted of a cylindrical aluminum disk with a depression of 3 mm in diameter into which the solid sample was filled and compressed into a pellet by applying a definite and reproducible pressure. The sample cell was mounted in a thermostatically controled aluminum block. In order to monitor the thermal degradation of the poly(aryl vinyl sulfoxides), the sample, as prepared in the above manner, was heated to the desired temperature, and Raman spectra were recorded on-line at intervals of 1–3 min.

Preparation of Substituted Aryl Vinyl Sulfides (7a–c). In a 1 L round-bottom flask fitted with a condenser, dropping funnel, and inert gas inlet, 1 mol of arenethiol (**4a–c**) was slowly added with stirring to a solution of 68.05 g (1 mol) of sodium ethoxide in 400 mL of ethanol. Stirring was continued for another 20 min, and the resulting mixture, containing the corresponding arenethiolate, was added to a solution of 272.4 g (1.45 mol) of 1,2-dibromoethane in 280 mL of ethanol. The temperature was maintained at 25–30 °C and, after 30 min, an ethanolic solution of 136.1 g (2 mol) of sodium ethoxide was added. Stirring was continued for 30 min, and then the reaction medium was heated under reflux for 8–12 h. After cooling to room temperature, the mixture was extracted with 750 mL of diethyl ether and 750 mL of water. The two layers were separated, and the aqueous layer was washed twice with 250 mL of diethyl ether. The combined organic layers were washed with 250 mL of saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The residue was distilled to give the pure aryl vinyl sulfides **7a–c**.

***p*-Fluorophenyl Vinyl Sulfide (7a):** yield 57%; ^{1}H-NMR (CDCl$_3$) δ 5.21 (d, J = 15 Hz, 1 H, 2-H$_{trans}$), 5.31 (d, J = 12 Hz, 1 H, 2-H_{cis}), 6.46 (dd, J = 15 Hz, J' = 12 Hz, 1 H, 1-H), 7.19 (AA′BB′, $\Delta\nu_{AB}$ = 145.5 Hz, 4 H, arom H); ^{13}C-NMR ($CDCl_3$) δ = 114.6 (C-2), 116.35 (*o*-F-C_{arom}), 128.8 (C_{arom}—S), 132.4 (C-1), 133.5 (*m*-F—C_{arom}), 162.47 (161.2 and 163.7; C_{arom}—F); MS *m/z* 154 (10) (M^+), 141 (100), 127 (92), 83 (60), 45 (58); IR (cm^{-1}) 1591, 1490 (C═C_{arom}), 1230, 1157, 1093 (aryl—F), 958, 882 (1,4-disubstituted aryl group), 828 (C—S—C). Anal. Calcd for C_8H_7SF (154.2): C, 62.3; H, 4.6. Found: C, 62.4; H, 4.7.

***p*-Chlorophenyl Vinyl Sulfide (7b):** yield 69%; ^{1}H-NMR ($CDCl_3$) δ 5.43 (m, 2 H, C═CH_2), 6.46 (dd, J = 16 Hz, J' = 14 Hz, 1 H, SC*H*═C), 7.22–7.37 (m, 4 H, arom H); ^{13}C-NMR ($CDCl_3$) δ 116.2, 129.3, 131.3, 131.7, 132.4, 132.8; MS *m/z* 170 (20) (M^+), 157 (100), 143 (71), 108 (75), 45 (60); IR (cm^{-1}) 1587, 1476 (C═C_{arom}), 1096, 1012 (aryl—Cl), 959, 882 (1,4-disubstituted aryl group), 817 (C—S—C). Anal. Calcd for C_8H_7SCl (170.7): C, 56.3; H, 4.1. Found: C, 56.3; H, 4.2.

***p*-Methoxyphenyl Vinyl Sulfide (7c):** yield 63%; ^{1}H-NMR ($CDCl_3$) δ 3.81 (s, 3 H, OCH_3), 5.09 (d, J = 16.6 Hz, 1 H, 2-H_{trans}), 5.21 (d, J = 9.3 Hz, 1 H, 2-H_{cis}), 6.43 (dd, J = 16.6 Hz, J' = 9.3 Hz, 1 H, 1-H), 7.10 (AA′BB′, $\Delta\nu_{AB}$ = 98.4 Hz, J_{AB} = 10 Hz, 4 H, arom H); MS *m/z* 182 (58) (M^+), 155 (100), 153 (39), 139 (57), 45 (25); IR (cm^{-1}) 1592, 1494 (C═C_{arom}), 1286, 1246 (aryl—OMe), 1031 (1,4-disubstituted aryl group), 827 (C—S—C). Anal. Calcd for $C_9H_{10}SO$ (166.2): C, 65.0; H, 6.1. Found: C, 65.0; H, 6.0.

Oxidation of the Aryl Vinyl Sulfides 7a–c to the Corresponding Sulfoxides 8a–c. A 5.1 g sample of 30% aqueous hydrogen peroxide (45 mmol) was slowly added to a mixture of 45 mmol of **7a–c** in 150 mL of glacial acetic acid and 2.3 mmol of sodium tungstate. The temperature was maintained at 20–25 °C by cooling with an ice bath. The reaction was monitored by TLC until the starting material had completely disappeared. The reaction was quenched by adding 100 mL of water, and the resulting mixture was extracted twice with 150 mL of dichloromethane. The combined organic layers were washed with 250 mL of saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*. Distillation of the residue gave the desired aryl vinyl sulfoxides **8a–c**, which were further purified by 3-fold distillation from calcium hydride.

***p*-Fluorophenyl Vinyl Sulfoxide (8a):** yield 75%; ^{1}H-NMR ($CDCl_3$) δ 6.00 (m, 1 H, 2-H_{trans}), 6.23 (m, 1 H, 2-H_{cis}), 6.59 (m, 1H, 1-H), 7.45 (AA′BB′, $\Delta\nu_{AB}$ = 172 Hz, 4 H, arom H); ^{13}C-NMR ($CDCl_3$) δ 116.7, 121.0, 127.2, 130.9, 142.9, 164.4; MS *m/z* 170 (16) (M^+), 143 (56), 122 (100), 95 (44), 75 (28); IR (cm^{-1}) 1589, 1491 (C═C_{arom}), 1085 (aryl—F), 1053 (R_2S═O), 959, 835 (1,4-disubstituted aryl group), 745 (C—S—C); UV ($CHCl_3$) λ_{max} 270 nm (sh). Anal. Calcd for C_8H_7SOF (170.2): C, 56.5; H, 4.2. Found: C, 56.5; H, 4.1.

***p*-Chlorophenyl Vinyl Sulfoxide (8b):** yield 79%; ^{1}H-NMR ($CDCl_3$) δ 5.35 (d, J = 17.3 Hz, 1 H, 2-H_{trans}), 5.40 (d, J = 12.3 Hz, 1 H, 2-H_{cis}), 6.52 (dd, J = 17.3 Hz, J' = 12.3 Hz, 1 H, 1-H), 7.32 (m, 4 H, arom H); ^{13}C-NMR ($CDCl_3$) δ 121.2, 126.1, 129.5, 129.7, 137.6, 142.8; MS *m/z* 186 (15) (M^+), 159 (56), 138 (100), 111 (31), 75 (38); IR (cm^{-1}) 1577, 1475 (C═C_{arom}), 1089 (aryl—Cl), 1053, 1012 (R_2S═O), 958, 825 (1,4-disubstituted aryl group), 770 (C—S—C); UV ($CHCl_3$) λ_{max} 266 nm (sh). Anal. Calcd for C_8H_7SOCl (186.7): C, 51.5; H, 3.8. Found: C, 51.5; H, 3.8.

***p*-Methoxyphenyl Vinyl Sulfoxide (8c):** yield 78%; ^{1}H-NMR ($CDCl_3$) δ 3.83 (s, 3 H, OCH_3), 5.90 (d, J = 10.6 Hz, 1 H, 2-H), 6.18 (d, J = 16 Hz, 1 H, 2-H), 6.60 (dd, J = 16 Hz, J' = 10.6 Hz, 1 H, 1-H), 7.30 (AA′BB′, $\Delta\nu_{AB}$ = 113 Hz, J_{AB} = 8 Hz, 4 H, arom H); ^{13}C-NMR ($CDCl_3$) δ 55.55, 115.0, 120.2, 127.2, 130.1, 142.9, 162.3; MS *m/z* 182 (8) (M^+), 155 (48), 134 (100), 123 (12), 77 (12); IR (cm^{-1}) 1593, 1496 (C═C_{arom}), 1255 (aryl—OMe), 1051 (R_2S═O), 1026, 831 (1,4-disubstituted aryl group); UV ($CHCl_3$) λ_{max} 267 nm (sh). Anal. Calcd for $C_9H_{10}SO_2$ (182.2): C, 59.3; H, 5.5. Found: C, 59.3; H, 5.5.

Preparation of the Poly(aryl vinyl sulfoxides) 9a–c by Polymerization of 8a–c. Under strictly oxygen- and moisture-free conditions, *sec*-butyllithium (solution in hexane; 1.4 M) was slowly added dropwise to a solution of 0.11 g (0.6 mmol) of 1,1-diphenylethylene in 15 mL of THF until the red color remained for at least 15 min. Subsequently, another 0.6 mmol of *sec*-butyllithium was added at room temperature, and the mixture was cooled to −78 °C. The desired monomer (**8a–c**, 36 mmol) was added and the temperature maintained at −78 °C for another 30 min. The reaction was quenched by addition of 0.2 mL (5 mmol) of deoxygenated methanol and the mixture allowed to warm to room temperature. The corresponding polymer (**9a–c**) was precipitated by addition of diethyl ether (200 mL) and dried *in vacuo*.

Poly(*p*-fluorophenyl vinyl sulfoxide) (9a): yield 67%; ^{1}H-NMR ($CDCl_3$) δ 1.3–2.1 (m, 2 H, −CH_2−), 2.9–3.5 (m, 1H, CH—S), 6.9–7.7 (m, 4 H, arom H); IR (cm^{-1}) 3060 (CH_{arom}), 2956 (CH), 1589, 1492 (C═C_{arom}), 1084 (aryl—F), 1045 (R_2S═O), 836 (1,4-disubstituted aryl group); M_w 10 435.

Poly(*p*-chlorophenyl vinyl sulfoxide) (9b): yield 81%; ^{1}H-NMR ($CDCl_3$) δ 2.2 (m, 2 H, −CH_2−), 3.5–3.6 (m, 1 H, C*H*—S), 7.2–7.7 (m, 4 H, arom H); IR (cm^{-1}) 3080 (CH_{arom}), 2960 (CH), 1581, 1475 (C═C_{arom}), 1091 (aryl—Cl), 1046, 1012 (R_2S═O), 827 (1,4-disubstituted aryl group), 7761 (C—S—C); M_w 12 018.

Poly(*p*-methoxyphenyl vinyl sulfoxide) (9c): yield 72%; ^{1}H-NMR ($CDCl_3$) δ 1.5–2.0 (m, 2 H, −CH_2−), 2.8–3.4 (m, 1 H, C*H*—S), 3.7–3.8 (m, 3 H, OCH_3), 6.7–7.8 (m, 4 H, arom H); IR (cm^{-1}) 2970 (CH_{arom}), 2920 (CH), 1594, 1497 (C═C_{arom}), 1258 (aryl—OMe), 1042 (R_2S═O), 1027, 832 (1,4-disubstituted aryl group); M_w 10 358.

Conclusion

all-trans-Polyacetylene is accessible by a novel synthesis based on the thermolysis of substituted poly(aryl vinyl sulfoxides). The rate of the reaction is significantly influenced by the particular substituent at the aromatic ring of the sulfoxide. Near-infrared-excited FT-Raman spectroscopy proved to be a suitable tool for the on-line monitoring of the reaction, and kinetic data on the formation of polyacetylene from various polymeric sulfoxide precursors could be determined by this technique.

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