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The thermal conversion reaction of sulphonyl substituted poly(*para*-xylylene): evidence for the formation of PPV structures

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Abstract

The thermal elimination of the *n*-octyl-sulphonyl group from poly[1,4 phenylene (1-*n*-octyl-sulphonyl)-1,2-ethylene] and the phenyl-sulphonyl group from poly[1,4 phenylene (1-phenyl-sulphonyl)-1,2-ethylene] is evaluated by different analytical techniques: thermal gravimetric analysis, direct insert probe mass spectrometry, in situ ultraviolet–visible spectroscopy and in situ Fourier transform infra red spectroscopy. This thermal treatment yields PPV with improved optical properties compared to the conventional PPV concerning UV-absorption and photoluminescence efficiencies. The results obtained are consistent with the formation of a PPV with a more or less restricted conjugation length compared to the PPV material obtained from the conversion of a sulphinyl precursor polymer. © 2002 Published by Elsevier Science Ltd.

Keywords: Poly(*para*-xylylene); PPV; Sulphonyl precursor polymers

1. Introduction

In the course of our work towards precursor routes for PPV derivatives, we were able to synthesise sulphonyl substituted poly(*para*-xylylene) derivatives. Initially this work was undertaken to achieve a deeper understanding in the in situ polymerisation behaviour of *p*-quinodimethane systems [1]. As these sulphonyl functional groups are thermally far more stable than the sulphinyl groups, which find application in the actual precursors towards PPV [2], the former were best suited to be used in initial mechanistic studies. The same chemistry also allowed the synthesis of formal 'copolymers' of sulphonyl and sulphinyl substituted poly(*para*-xylylene) derivatives [3], which opens a route towards conjugated polymers with specific effective conjugation lengths. In the course of the study of thermal stability of the sulphonyl homopolymers, a final degradation temperature (496 °C) was observed in thermal gravimetric analysis (TGA) which is almost identical with the degradation temperature of PPV. Also in direct insert probe mass spectrometry (DIP-MS) the fragments observed were consistent with the formation of PPV. This would imply that these sulphonyl functionalities although thermally far more stable compared to other functional groups used towards precursors for conjugated polymers in the end, still should give rise to the formation of PPVs. Intriged by this possibility, we decided to investigate the thermal stability of *n*-octyl- and phenyl-sulphonyl substituted poly(*para*-xylylenes) in more detail with in situ Fourier transform infra red spectroscopy (FT-IR) spectroscopy and in situ ultraviolet–visible (UV–vis) spectroscopy. After elimination the optical properties of the conjugated polymers obtained, were analysed by photoluminescence spectroscopy and also photoluminescence efficiencies were determined.

2. Results and discussion

2.1. Synthesis of sulphonyl substituted poly(*para*-xylylenes)

Synthesis of the alkyl-sulphonyl poly(*para*-xylylenes) by oxidation of the alkyl-sulphinyl macromolecule is performed by the use of *meta*-chloroperbenzoic acid in CH_2Cl_2. This oxidation has no effect on the molecular weight as determined by gel permeation chromatography

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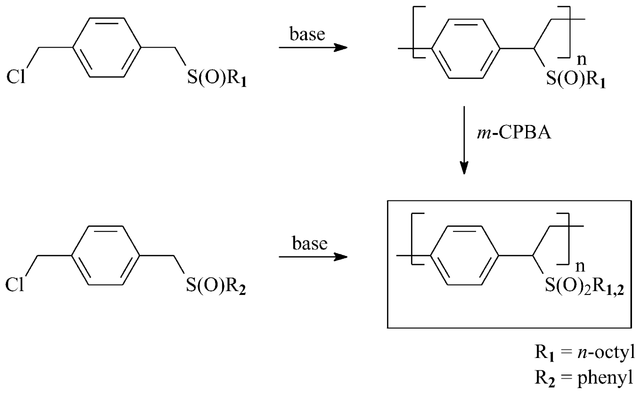


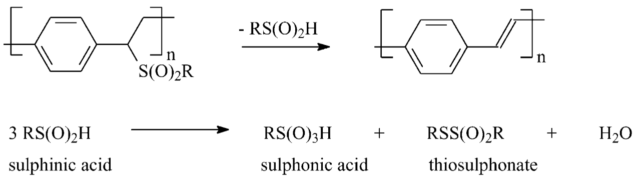
Scheme 1. Synthesis of sulphonyl polymers by different methods.

(GPC) against polystyrene standards [1]. Because of the instability of the phenyl-sulphinyl poly(*para*-xylylene) [4], the phenyl-sulphonyl poly(*para*-xylylene) is synthesised by polymerisation of the phenyl-sulphonyl premonomer (Scheme 1).

2.2. Thermal behaviour of sulphonyl substituted poly(*para*-xylylenes) studied by TGA and DIP-MS

The sulphonyl polymers (R = *n*-octyl and R = phenyl) show two distinct temperature ranges of weight loss in TGA. At about 300 °C, related to the elimination of the sulphonyl functional group and at about 450 °C pointing to the degradation of the material formed (Table 1).

DIP-MS was used to obtain information about the structure of the elimination products. In this technique, the material which is to be examined is brought directly to the heating element of the probe from solution as a thin film and this enables to study the fragments that are liberated in high vacuum (10^{-6} mm Hg) inside the spectrometer upon elimination and degradation. Liberated fragments were ionised by electron impact (70 eV) and a heating rate for the probe of 10 °C/min was imposed comparable to the TGA experiments. In accordance with the TGA measurements, two signals were observed in a reconstructed ionogram, which can be assigned to an elimination and degradation step on the basis of the fragments observed. This is indicated in Table 2 for the elimination step. Chemical ionisation (CI) has the advantage of showing the initial species formed before further fragmentation in the probe. The decrease in elimination and degradation temperature compared with TGA most probably is the consequence of the high vacuum in the probe (Table 1), which results in faster evaporation of the elimination products.



Scheme 2. Thermolysis of sulphonyl precursor polymers.

For the *n*-octyl-sulphonyl polymer confirmation of assignment for the underlined *m*/*z* (DIP-EI) values was obtained by means of high-resolution DIP-MS mass, which enables calculation of elemental composition. The collection of data presented in Table 2 is consistent with the formation of sulphinic acid as eliminating group and would imply the formation of a double bond and thus PPV. This sulphinic acid is known to dimerise and disproportionate likewise sulphenic acids yielding a thiosulphonate and a sulphonic acid [7,8] (Scheme 2). Whether the sulphinic acid is formed via a concerted or radical pathway is out of scope of the data presented. It has been suggested that sulphonyl groups on a polymer backbone might be converted to double bonds at higher temperature [5,6], but to the best of our knowledge no evidence was ever provided for polymers.

2.3. Thermal behaviour of sulphonyl substituted poly(*para*-xylylenes) studied by in situ FT-IR and UV–vis

To obtain more detailed information on the processes occurring at increasing temperatures we turned to in situ UV–vis and FT-IR spectroscopy. The latter showed to be very useful in the analysis of the elimination process of sulphinyl and xanthate precursors towards PPV [9,10]. For all experiments we used a high temperature cell, which can be inserted in the sample compartment of the UV–vis and FT-IR spectrometer. Films of substituted poly(*para*-xylylenes) on quartz or KBr pellets were spincoated from solution.

An in situ elimination reaction was performed at the rate of 2 °C/min from an ambient temperature up to 350 °C

Table 1
Elimination and degradation temperature derived from TGA and DIP-MS (heating rate 10 °C/min)

Precursor polymer	TGA (°C)[a]		DIP-MS (°C)[b]	
	Elimination	Degradation	Elimination	Degradation
n-Octyl-sulphinyl	284	573	168	411
n-Octyl-sulphonyl **1**	329	472	285	335
Phenyl-sulphonyl **2**	283	437	250	380

[a] Ambient pressure (nitrogen flow).
[b] Under vacuum (10^{-6} mm Hg).

Table 2
Comparison of the thermolysis of sulphonyl polymers

n-Octyl-sulphonyl		Phenyl-sulphonyl	
m/z	Fragment	*m/z*	Fragment
DIP-EI			
290	$C_8H_{17}SSC_8H_{17}^{+}$	250	$C_6H_5SO_2SC_6H_5^{+}$
161	$C_8H_{17}SO^{+}$	218	$C_6H_5SO_2C_6H_5^{+}$
145	$C_8H_{17}S^{+}$	158	$C_6H_5SO_3H^{+}$
114	$C_8H_{18}^{+}$	142	$C_6H_5SO_2H^{+}$
113	$C_8H_{17}^{+}$	141	$C_6H_5SO_2^{+}$
112	$C_8H_{16}^{+}$	125	$C_6H_5SO^{+}$
85	$C_6H_{13}^{+}$	109	$C_6H_5S^{+}$
71	$C_5H_{11}^{+}$	94	$C_6H_5OH^{+}$
64	SO_2^{+}	77	$C_6H_5^{+}$
57	$C_4H_9^{+}$	64	SO_2^{+}
48	SO^{+}		
DIP-CI			
291	$[C_8H_{17}SSC_8H_{17}]H^{+}$	251	$[C_6H_5SO_2SC_6H_5]H^{+}$
259	$[C_8H_{17}SC_8H_{17}]H^{+}$	219	$[C_6H_5SO_2C_6H_5]H^{+}$
162	$[C_8H_{17}SO]H^{+}$	143	$[C_6H_5SO_2H]H^{+}$
146	$[C_8H_{17}S]H^{+}$	127	$[C_6H_5SOH]H^{+}$
113	$[C_8H_{16}]H^{+}$		

Underlined fragment ions are confirmed by HR-MS.

under a continuous flow of nitrogen for *n*-octyl as well as phenyl-sulphonyl poly(*para*-xylylene). For comparison, we also present the corresponding data for the *n*-octyl-sulphinyl poly(*para*-xylylene) [2]. During elimination from precursor to a conjugated polymer, the formation of the *trans* vinylene double bond is observed at 960 cm^{-1} and simultaneously the sulphonyl frequencies disappear (not shown). Indeed around 1300 cm^{-1} an absorption band is visible which is due to stretching of the sulphonyl group [11]. Another band is found at about 1130 cm^{-1} for the *n*-octyl-sulphonyl and 1144 cm^{-1} for the phenyl-sulphonyl. For the sulphinyl group, the corresponding absorption band is visible at 1048 cm^{-1}. From Fig. 1, which shows the increase of the *trans* vinylene double bond signal at 960 cm^{-1} as a function of increasing temperature, it becomes clear that elimination for both the *n*-octyl- and phenyl-sulphonyl poly(*para*-xylylene) leads to PPV in a similar way as for the sulphinyl poly(*para*-xylylene), but in a temperature range (250–330 °C) much higher than for the latter (70–120 °C). After these temperatures, 330 and 120 °C, neither sulphonyl nor sulphinyl functionalities are present anymore in the corresponding precursors. Fig. 1 also seems to indicate that the conjugated PPV polymer obtained from the *n*-octyl-sulphonyl poly(*para*-xylylene) shows lower thermal stability of the conjugated system compared to the PPV polymer obtained from the phenyl-sulphonyl poly(*para*-xylylene). An additional experiment with isothermal heating at 330 °C for 2 h shows that the absorbance at 960 cm^{-1}, for the *trans* vinylene double bond, slightly decreases for the *n*-octyl and stays unchanged for the phenyl substituent. Thus confirming the earlier observation of a higher thermal stability of the PPV material derived from the phenyl-sulphonyl derivative. These observations may point to the difference in structure of the PPV materials obtained, which may be related to the difference in the number of defects.

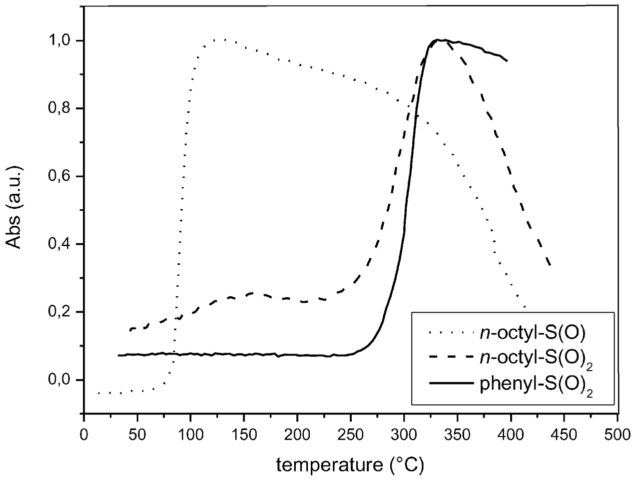


Fig. 1. Absorbance of the *trans* vinylene double bond signal at 960 cm^{-1} as a function of temperature.

More specific, the results obtained seem to indicate that the PPV polymer resulting from the conversion of the *n*-octyl-sulphonyl poly(*para*-xylylene) has a less well defined structure than the PPV material obtained from the phenyl-sulphonyl substituted poly(*para*-xylylene).

The UV–vis absorption is due to a $\pi-\pi^*$ transition in the conjugated backbone of PPV and is dependent on the 'effective' conjugation length [12–18]. In situ UV–vis spectroscopy can be used to monitor the development of the effective conjugation length as a function of temperature. The ultimate value of the maximum absorption thus

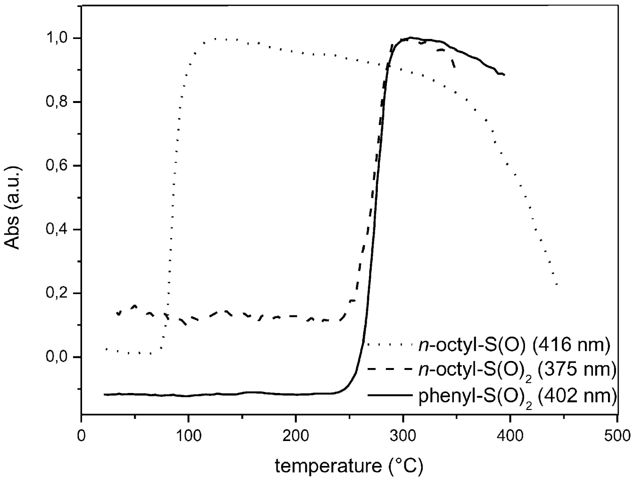


Fig. 2. Absorbance of the maximum absorption of the conjugated system as a function of temperature.

obtained can be interpreted as a measure of 'extension of conjugation'. Spincoated films of substituted poly(*para*-xylylenes) on quartz plates (± 100 nm) are eliminated in the same high temperature cell which is placed in the beam of the UV–vis spectrophotometer. During elimination there is a continuous red shift. In the first part smaller conjugated segments are formed but at higher extent of elimination the absorption band becomes broad. Each precursor polymer is heated at 2 °C/min from ambient temperature up to ~400 °C under a continuous flow of nitrogen. To monitor the elimination process, the absorbance of the maximum absorption is plotted as a function of temperature (Figs. 2 and 3). Results are summarised in Table 3. The conversion of a *n*-octyl-sulphinyl poly(*para*-xylylene) is shown as a reference, because it has been established before, that after elimination, pristine PPV is obtained ($\lambda_{max} = 416$ nm) [2].

If the UV-absorption bands of the eliminated *n*-octyl-sulphinyl poly(*para*-xylylene) and the eliminated phenyl-sulphonyl poly(*para*-xylylene) ($\lambda_{max} = 402$ nm) are compared (Fig. 4), almost identical absorption bands can be observed except from the value of λ_{max} which is for the phenyl-sulphonyl poly(*para*-xylylene) slightly blue-shifted (14 nm). Nevertheless, the conjugated polymer obtained from a phenyl-sulphonyl poly(*para*-xylylene) precursor is still identical and even better in view of λ_{max} compared to the PPV polymer obtained from a xanthate PPV precursor polymer ($\lambda_{max} = 396$ nm) [9,10].

Table 3
Data results concerning the elimination process

	λ_{max} (nm)	Elimination temperature (°C)	λ_{max}-Emission (nm)	PL-efficiency (%)
n-Octyl-sulphonyl **1**	375	250–300	502	12
n-Phenyl-sulphonyl **2**	402	250–307	554	11
n-Octyl-sulphinyl	416	70–120	552	7

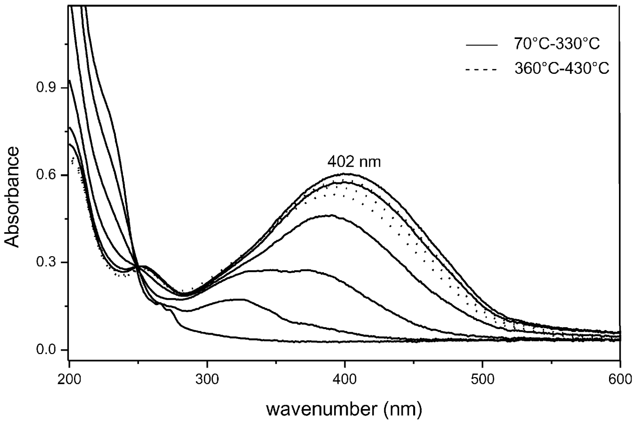


Fig. 3. UV-absorption spectra obtained from the phenyl-sulphonyl precursor polymer (··· red-shift = elimination; - - - blue-shift = degradation).

The conjugated polymer obtained from the conversion of the *n*-octyl-sulphonyl poly(*para*-xylylene) with a $\lambda_{max} = 375$ nm is strongly blue-shifted, suggesting a much smaller effective conjugation length (Fig. 5). The finestructure, visible for the absorption band of the eliminated *n*-octyl-sulphonyl PPV polymer, and due to the various vibrational levels, confirm the presence of shorter conjugated units. This limited effective conjugation length points to the presence of a substantial amount of structural defects in this material. These results substantiate the relation assumed between thermal instability and the presence of structural defects or irregularities in the material. Fig. 3 also shows that the starting point for the elimination process derived from UV–vis measurements is in excellent agreement with the data determined with FT-IR spectroscopy, proving that both techniques give complementary information.

From the shape of the PL spectra and the maxima observed it is clear that the conjugated system of PPV obtained from a *n*-octyl-sulphonyl precursor consists of

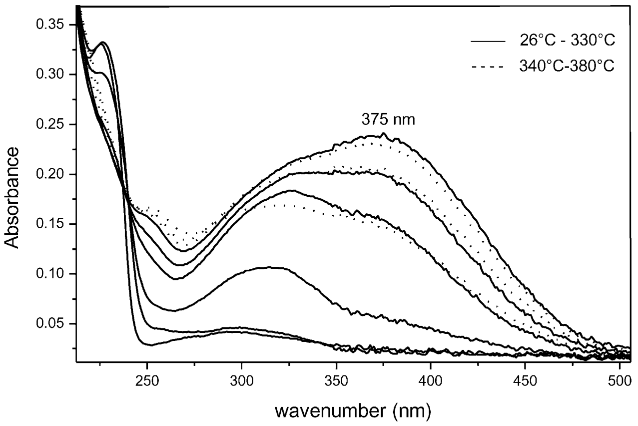


Fig. 4. UV-absorption spectra obtained from *n*-octyl-sulphonyl precursor polymer at different increasing temperatures (— red-shift = elimination; - - - blue-shift = degradation).

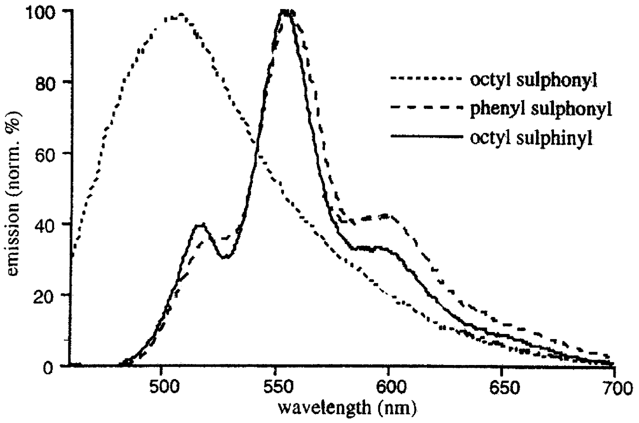


Fig. 5. Normalised photoluminescence of eliminated sulphonyl precursors and a *n*-octyl-sulphinyl precursor (350 °C, 30 min, 0.2 mbar) excitation wavelength: 430 nm.

small conjugated fragments (Fig. 5) [20]. The fact that the alkyl-sulphonyl poly(*para*-xylylene) yields PPV, in which only one emission band is visible, indicates a restricted conjugation length. The spectrum of the eliminated phenyl-sulphonyl poly(*para*-xylylene), however, is almost identical to the PPV obtained from the sulphinyl poly(*para*-xylylene) [9,10]. Results are summarised in Table 3. The efficiencies of photoluminescence are higher than for PPV, synthesised via the sulphinyl-route, which shows efficiencies between 4 and 8%, depending on elimination conditions and substituent R-groups on the sulphinyl group. These higher efficiencies are assumed to be related to an interrupted conjugated system, even in the case of the PPV derived from the phenyl-sulphonyl precursor [3]. Whether this points to defects in the conjugation formed during the conversion process or by incomplete elimination cannot be established.

3. Conclusion

PPV can be formed out of the thermal conversion of alkyl- or phenyl-sulphonyl substituted poly(*para*-xylylene). The PPV that springs from an alkyl-sulphonyl poly(*para*-xylylene) has optical properties which are quite different from the PPV derived from the phenyl-sulphonyl poly(*para*-xylylene), and must be viewed as deteriorating. However, the phenyl-sulphonyl derivative yields PPV, which is almost identical to PPV obtained from sulphinyl PPV precursors.

4. Experimental section

4.1. General remarks

The TGA-measurements were performed on a TA Instrument 951 Thermogravimetric Analyser with a continuous argon-flow of 80 ml/min. Samples of poly(*para*-xylylenes) were inserted in the solid state. HR-DIP-MS was recorded at Akzo Nobel Corporate Research Arnhem on a double focussing magnetic sector instrument, Finnigan MAT 900, electron energy 70 eV. Brute formulas are derived from *m*/*z* calibrated with a perfluorokerosine mixture. DIP-MS analysis is carried out on a Finnigan TSQ 70, electron impact mode, mass range 35–550 and scan rate of 2 s. Electron energy is 70 eV. A $CHCl_3$ solution of polymer is applied on the heating element of the probe. Deviation in actual temperature from the heating program was 6 °C at maximum. GPC is performed on a Spectraseries P100, Spectra Physics with a 10 mm mixed B 300 $*$ 7.5 mm column equipped with a refractometer as detector. The molecular weights are determined in DMF as eluent and against polystyrene standards.

Purification of monomers by column chromatography is performed on Merck silica gel 60. Thin layer chromatography (TLC) was carried out on silica gel 60 F254 plates. Photoluminescence spectra are recorded at the Philips Research Laboratories on a Perkin Elmer LS 50 Luminescence Spectrometer using an excitation of 430 nm. The photoluminescence efficiency is determined in a set-up, built by Dr A. Berntsen with a calibrated integrating sphere. A correction is performed for the spectral dependencies of the luminescence, the collection optics and reflection at the sample surface. Rhodamine 101 was used as reference for the efficiencies and a laser light of 355 nm was used for excitation. The in situ elimination reactions are performed in a Harrick high temperature cell from Safir, which is positioned in the beam of a Perkin Elmer Spectrum one FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans). The temperature of the sample and the metal part is controlled by a Watlow (serial number 999, dual channel) temperature controller. A poly(*para*-xylylene) was spin-coated from a $CHCl_3$ solution (6 mg/ml) on a KBr pellet at 500 rpm. The spincoated KBr pellet (diameter 25 mm, thickness 1 mm) is in contact with the metal part. A background spectrum is recorded before heating and continuous scanning is started. All experiments were done at 2 °C/min under a continuous flow of nitrogen. 'Timebase software', supplied by Perkin Elmer, is used to integrate the regions of interest.

The in situ UV–vis spectroscopy is performed on a Cary 500 UV–vis–NIR spectrophotometer (interval 1 nm, scan rate 600 nm/min, continuous run from 200 to 700 nm). A poly(*para*-xylylene) was spincoated from a $CHCl_3$ solution (6 mg/ml) on a quartz plate at 700 rpm. The spincoated quartz plate (diameter 25 mm, thickness 3 mm) was heated in the same high temperature cell as used for the FT-IR measurements. This high temperature cell is also positioned in the beam of the UV–vis–NIR spectrophotometer, specially adopted to contain the Harrick high temperature cell. A background spectrum is recorded before heating and continuous scanning is started at 2 °C/min under a continuous flow of nitrogen. 'Scanning Kinetics software', supplied by Varian, is used to integrate the regions of interest.

4.2. Monomers

The *n*-octyl-sulphinyl monomer was synthesised and polymerised as described before [19] and afterwards oxidised to the sulphonyl. The phenyl-sulphonyl polymer **2** was synthesised by polymerisation of the sulphonyl monomer.

4.2.1. 1-((Chloro methyl) methyl-4-(phenyl-sulphonyl)benzene

Mp: 170.3–170.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (q, 2H, SO_2*Ph*), 7.44 (t, 2H, SO_2Ph), 7.26 (d, 2H, *Ph*CH_2SO_2Ph), 7.07 (d, 2H, *Ph*CH_2SO_2Ph), 4.28 (s, 2H, PhC*H*$_2SO_2$Ph), 4.52 (s, 2H, PhC*H*$_2$Cl); MS (70 eV, EI): 280 (M^+), 245 (M − Cl), 139 (M − $S(O)_2$Ph), 104 (CH_2–Ph–CH_2), 77 (C_6H_5); IR (KBr, cm^{-1}): 3053 (C–H benzene stretch in-plane), 2950 (CH_2 asymm. stretch), 1609, 1583 (both C–C benzene ring-stretch), 1515, 1443, 1410 (all semi-circle stretching benzene), 1290 (sulphone asymm. stretch), 1150 (sulphone symm. stretch), 1084 (semi-circle ring-stretch phenyl group), 1020 (benzene C–C vibration), 930 (out-of-plane wag benzene), 845 (1,4 disubstitution *p*-phenylene CH out-of-plane wag), 750 (phenyl 5 adjacent Hs), 722 (out-of-plane sextant ring bend vibration benzene), 688 (ring bend phenyl), 662 (benzylic chloride), 608 (sulphone scissors deformation), 539 (out-of-plane quadrant ring bending phenyl group), 508 (sulphone wag).

NMR characteristics of sulphinyl monomers and a general procedure for monomer synthesis have been described in a previous paper [20].

4.2.2. Poly[*para*-phenylene (1-phenyl-sulphonyl)-ethylene]

General procedure for the polymerisation.

The 1-((chloro methyl) methyl-4-(phenyl-sulphonyl)-benzene was polymerised in 55% yield in CH_2Cl_2.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.0 (5H, SO_2Ph), 6.8–6.6 (4H, CH_2PhCH_2), 4.15–3.9 (Ph–C*H*–), 3.6 (1H, PhCH–C*H*$_2$), 3.15 (1H, Ph–CHC*H*$_2$); $\bar{M}_n$ 3,400,000, $\bar{M}_w$: 2,900,000, IR: 3060 (aromatic C–H stretch), 2955 (CH_2 asymm. stretch), 2927 (CH_2 asymm. stretch), 2870 (CH_2 asymm. stretch), 1558 (ring-stretch phenyl group, opposite quadrants), 1515 (semi-circle stretch phenyl), 1446 (semi-circle stretching phenyl group), 1298 (SO_2 asymm. stretch), 1145 (SO_2 symm. stretch), 872 (quadrant in-plane-bending benzene), 827 (1,4 disubstituted *p*-phenylene CH out-of-plane bend), 758 (H-wag phenyl group 5 adjacent Hs), 688 (out-of-plane sextant ring bending phenyl group), 612 (SO_2 scissors deformation), 590 (SO_2 scissors deformation), 570 (*p*-phenylene out-of-plane), 505 (SO_2 wag); T_g is 117 °C.

Polymerisation of *n*-octyl-sulphinyl and phenyl-sulphonyl monomer were carried out as described before [21]. Alkyl-sulphinyl polymers were oxidised with *meta*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2.

4.2.3. General procedure for oxidation of a sulphinyl macromolecule

Polymer (0.4 mmol) was dissolved in dichloromethane (100 ml) under anhydrous conditions and cooled down to 0 °C before a solution of *m*-CPBA (4.8 mmol, 828 mg) was added dropwise. After 1 h at 0 °C the reaction mixture was stirred for another hour at room temperature. The organic phase was washed with water (3 ×) and washed with 0.1 M $NaHCO_3$ solution. The organic phase was concentrated in vacuo and the polymer was precipitated in a mixture of diethylether/hexane (1:1) from a solution of dichloromethane. Molecular weight is not changed by oxidation, i.e. the beginning sulphinyl precursor polymer has the exact molecular weight of the final sulphonyl polymer (*n*-octyl-sulphonyl: $M_n = 2 \times 10^5$, $M_w = 5 \times 10^5$; phenyl-sulphonyl: $M_n = 2 \times 10^5$, $M_w = 4 \times 10^5$). The change of hydrodynamic volume by a different polarity of side groups on the polymer is thus negligible. GPC was measured against PS standards and NMP was used as eluent.

4.3. IR frequencies (cm^{-1}) of the precursor polymers

*n-Octyl-sulphonyl (**1**)*: 2955 (CH_2 asymm. stretch), 2927 (CH_2 asymm. stretch), 2870 (CH_2 asymm. stretch), 1457 (C–H deformation), 1298 (SO_2 asymm. stretch), 1129 (SO_2 symm. stretch), 873 (quadrant in-plane-bending benzene), 829 (1,4 disubstituted *p*-phenylene CH out-of-plane bend), 612 (SO_2 scissors deformation), 570 (*p*-phenylene out-of-plane).

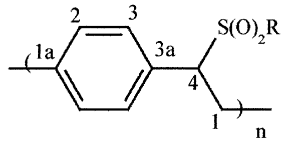
*Phenyl-sulphonyl (**2**)*: 3060 (aromatic C–H stretch), 2955 (CH_2 asymm. stretch), 2927 (CH_2 asymm. stretch), 2870 (CH_2 asymm. stretch), 1558 (ring-stretch phenyl group, opposite quadrants), 1515 (semi-circle stretch phenyl), 1446 (semi-circle stretching phenyl group), 1298 (SO_2 asymm. stretch), 1145 (SO_2 symm. stretch), 872 (quadrant in-plane-bending benzene), 827 (1,4 disubstituted *p*-phenylene CH out-of-plane bend), 758 (H-wag phenyl group 5 adjacent Hs), 688 (out-of-plane sextant ring bending phenyl group), 612 (SO_2 scissors deformation), 590 (SO_2 scissors deformation), 570 (*p*-phenylene out-of-plane), 505 (SO_2 wag).

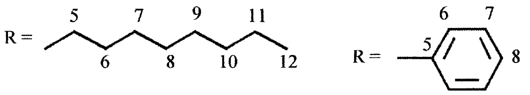
^{1}H NMR spectra were obtained in $CDCl_3$ at 400 MHz on a Varian Unity spectrometer using a 5 mm probe. Chemical shifts (δ) in ppm were determined relative to the residual $CHCl_3$ absorption (7.24 ppm). The ^{13}C NMR experiments were recorded at 100 MHz on the same spectrometer using a 5 mm broad-band probe. Chemical shifts were defined relative to the ^{13}C resonance shift of $CHCl_3$ (77.0 ppm).

Assignment of resonances was performed by the help of attached proton test by which the carbon multiplicity was determined and by comparison with the shifts of the monomers. These monomers were extensively studied and are described in a previous paper (Table 4) [22].

Table 4
^{13}C NMR and ^{1}H NMR for both sulphonyl poly(*para*-xylylenes)

^{13}C-NMR shift (ppm)
^{1}H-NMR shift (ppm)





C-1	33.44	32.86
C-1a	138.09	137.37
C-2	129.59	128.78
C-3	129.59	129.38
C-3a	130.00	129.83
C-4	69.06	71.76
C-5	50.70	136.46
C-6	33.44	128.42
C-7	31.57	128.70
C-8	28.35	133.39
C-9	22.48	–
C-10	21.40	–
C-11	21.23	–
C-12		
H-1	3.15	3.13
H-1′	3.66	3.66
H-2		
H-3	6.75–7.10	6.71
H-4	4.08	4.03
H-5	2.54	
H-6	1.66	7.11
H-7	1.54	7.27
H-8	1.20	7.36
H-9	1.20	–
H-10	1.20	–
H-11	1.20	–
H-12	0.78	–

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