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A GENERAL APPROACH TO PRECURSORS FOR POLY(ARYLENE VINYLENE) DERIVATIVES: MECHANISM, SCOPE AND MODIFICATIONS

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Abstract: A new precursor route for poly(arylene vinylene) derivatives will be presented. In this way non-ionic precursor polymers are obtained which show an enhanced thermal stability and are soluble in organic solvents. This enables a thorough structural characterization and the study of the mechanism. Experiments have been performed to differentiate between a radical or an ionic polymerization mechanism. Furthermore possibilities to tune solubility characteristics and to introduce defects in the polymer backbone will be discussed. Also the scope for this new route was explored. The first results indicate that the versatility exceeds that of the Wessling route, e.g. the synthesis of precursors for poly(*p*-biphenylene vinylene) and poly(2,6-naphthylene vinylene) could be accomplished in our case, whereas it failed in the case of the Wessling route.

INTRODUCTION

Precursor routes for conjugated materials are of great importance for the development of optical and electronic applications for organic semiconductors. They introduce processibility, which makes the incorporation of these materials into devices feasible. A precursor route that has shown to be very versatile, is the route introduced by Wessling and Zimmerman in the late 60's (Ref. 1a) and investigated thoroughly for this purpose by Lenz and Karasz in the beginning of the 80's (Ref. 2). Their precursor polymer can lead after thermal conversion to materials derived from Poly(p-Phenylene Vinylene) (PPV) derivatives with very good mechanical properties, high thermal stability, large conductivities, in some cases with a strong anisotropy (Ref. 3) and they have even shown great promise for the development of Polymeric Light Emitting Devices (P-LED's) (Ref. 4). Still there are some drawbacks, which are inherent to this route, e.g. instability of the precursor polymer and gel formation. These problems have been circumvented by Yamada et al. (Ref. 5) by substitution of the sulphonium groups in the precursor by alkoxy ether groups. Another limitation documented in the literature is the observation that monomers possessing enlarged aromatic systems, e.g. 4,4'-biphenylene

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or 2,6-naphthalene, show no tendency to polymerise in the circumstances used in the Wessling precursor route (Ref. 6).

Solutions may be found if the chemistry involved is understood in detail. In the case of the Wessling precursor route one is dealing with an example of the polymerization behaviour of *p*-quinodimethane systems, of which other examples can be found well before the 70's, e.g. the Gilch route (Ref. 7). In our work we have tried to define the prerequisites of such polymerization routes. To this end we have introduced a generalized scheme (Fig. 1) in which a clear distinction is made in the three steps of the process, first, the *in situ* formation of the actual monomer, the *p*-quinodimethane system (3), secondly, the polymerization reaction and thirdly the conversion to the fully conjugated system (5).

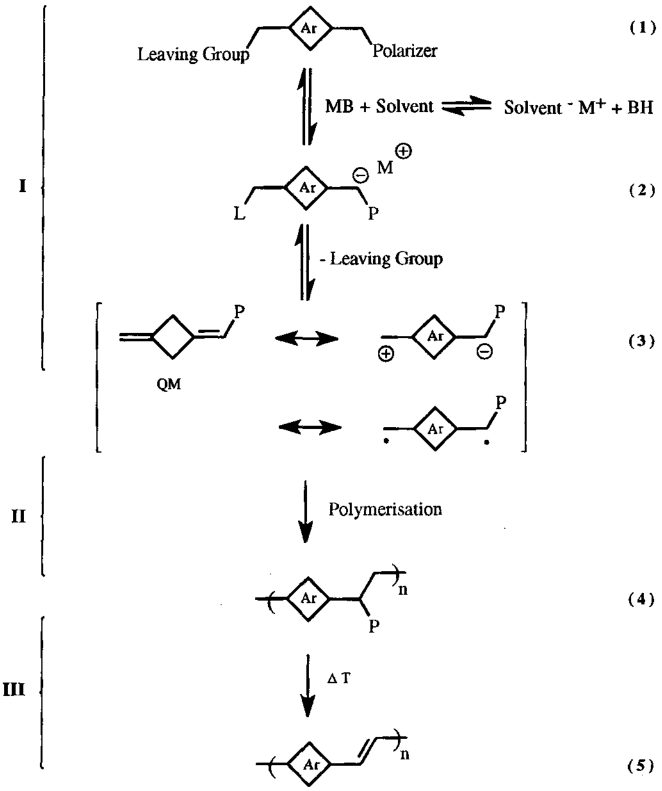


Figure 1. General Scheme

The *in situ* formation of the *p*-quinodimethane system as a consequence of a base induced elimination reaction, is possible if α,α'-functionalised *p*-xylene-derivatives (**1**), are used in which two requirements are fulfilled: (i) in the α-position of the *p*-xylene pre-monomer a polarizer is present, that can preferentially stabilize the anion formed in the first reaction step of the process, and (ii) a leaving group is needed in the α'-position to obtain the *p*-quinodimethane intermediate. The function of the polarizer is in fact threefold. The second function consists in polarizing the *p*-quinodimethane system in such a way that regular head to tail addition is guaranteed and thirdly it should offer a specific chemistry which allows for formation of a double bond.

One should stress that using chemically identical polarizers and leaving groups, e.g. the Wessling and Gilch routes, implies unstable precursor polymers. The demand to have an efficient monomer formation for efficient polymerization, leads to the use of good leaving groups, e.g. sulphonium or chloride substituents, which yield precursor polymers with highly reactive polarizers. The other way around, the wish to have a relatively stable precursor polymer implies a compromise in the leaving group capability and by consequence severe reaction conditions for the polymerization reaction. One way or the other using chemically identical polarizers and leaving groups imposes the same chemistry that applies on the monomer formation onto the precursor polymer. In conclusion, if the control on the polymerization process and the stability of the precursor polymers, is put forward as principal goals, there is a necessity for a chemical differentiation of the polarizer and leaving group. We have chosen to use halides as leaving groups because they have a high leaving group capability and do not enhance the acidity of the benzylic position. Sulfinyl groups introduce the opposite behaviour and show no leaving group properties vs. nucleophilic reagents, on the other hand the concerted thermal conversion to a double bond is well documented (Ref. 8). Furthermore the alkyl (or aryl) side chain which comes along with the sulfinyl group opens opportunities to tune the solubility characteristics of the precursor polymer. Previous work by us has shown that these type of monomers, e.g. α-alkyl(or aryl)sulfinyl- α'- chloride functionalised *p*-xylene-derivatives, yield high molecular weight precursor polymers soluble in simple organic solvents, which can be converted very conveniently to the fully conjugated polymer (Ref. 9). The stability at room temperature makes a thorough characterization using spectroscopic techniques and Gel Permeation Chromatography (GPC) possible, opening also opportunities to study the mechanism.

Four topics will be discussed in more detail:

I. The mechanism of the polymerization process.
II. Fine tuning of the solubility characteristics.
III. Possibilities for chemical modifications on the sulfinyl precursor.
IV. The polymerization of monomers with enlarged aromatic systems.

I. THE MECHANISM OF THE POLYMERIZATION PROCESS

In literature the polymerization of di-*p*-xylylene to poly(*p*-xylylene) is considered as a reaction with a diradical nature (Ref. 10a). The polymerization is initiated by the coupling of two *p*-xylylene molecules to form a diradical, which then grows by the addition of *p*-xylylene at both of its radical centres.

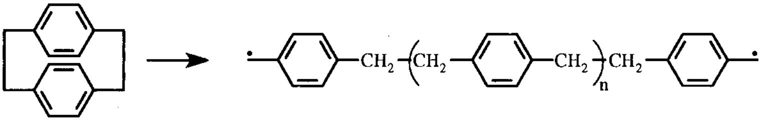


Figure 2. Polymerization of di-*p*-xylylene

The polymerization mechanism of the Wessling (and analogous) precursor route to PPV-derivatives, has been under discussion for several years (Ref. 2, 11). As stated above, the monomer in the latter polymerization reaction is also a *p*-xylylene derivative. Whether the reaction follows a radical or an anionic reaction path is still indefinite. Research on this mechanism has proven rather difficult because of the ionic nature of the precursor, making molecular weight and structure determinations hard to perform. Another difficulty is the instability of the precursor due to the good leaving capacity of the sulfonium groups (Ref. 11). As our precursor polymer (Ref. 9) carries a non-ionic sulfinyl group on the ethylene position, it is soluble in common organic solvents which simplifies it's characterization. Molecular weight determination can be performed in a straightforward way. This opens new perspectives to the study of the reaction mechanism of these type of premonomers.

In this chemistry, one should make a clear distinction between the two steps in the polymerization process: first, the formation of the *p*-quinodimethane system (**3**), and secondly, the polymerization reaction itself. In practice, it is almost impossible to investigate these two steps separately because the *p*-quinodimethane system (**3**), is not stable and thus can not be isolated. As a consequence it is difficult to distinguish between effects on the quinoid formation and effects on the polymerization itself. Two points concerning the mechanism of our route will be discussed, firstly the free radical nature of the polymerization reaction and secondly results concerning the formation of the quinoid structure itself.

We added radical trappers to the reaction mixture in order to reveal the character of the polymerization reaction. The radical trappers we used are 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and diphenylpicryl-hydrazyl (DPPH). TEMPO and DPPH are known as very strong inhibitors of free radical polymerizations. Adding more than 0.1 equivalents of these two trappers to the reaction system, totally inhibits the polymerization reaction. Adding smaller amounts of TEMPO or DPPH results in a substantial decrease of the molecular weight of the precursor polymer. Both observations are serious indications for a free radical mechanism of the polymerization reaction of α- sulfinyl -α'- chloro -*p*-xylene derivatives.

The reaction mixture formed in the case of total inhibition was investigated thoroughly by means of Nuclear Magnetic Resonance (NMR), Mass Spectrometry (MS) and Infra Red(IR)-spectroscopy. The mixture consisted in three products from which one could be identified as unreacted premonomer (**6a**) (R= n-butyl). The second component is formed via a side reaction of the polymerization (Fig. 3). The quinoid structure (7a) or the premonomer (**6a**) is attacked by a solvent anion resulting in a substitution of the leaving group by the solvent. The resulting product (**8a**) can not form a quinoid system under these circumstances, so it is unable to participate further in the polymerization. As a result this reaction will decrease the polymer yield. The third compound (**9**) gives us a clear hint towards the structure of the initiating species. This dialdehyde (**9**) can be formed only by the coupling of two quinoid structures (**7**). The resulting diradical will react with TEMPO, when this trapper is added. The formed dinitroxide is not very stable and can lead - by a rearrangement or hydrolysis - to the dialdehyde.

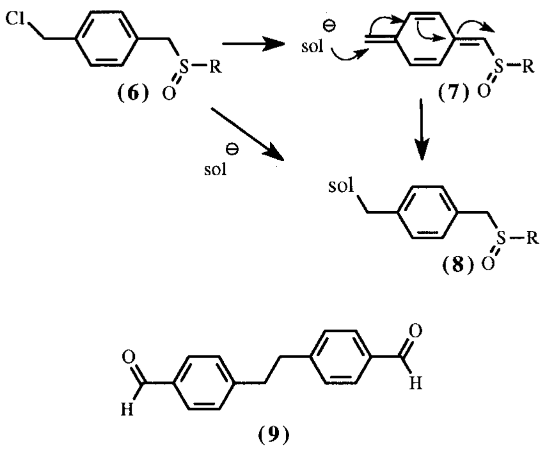


Figure 3. Solvent substitution on the monomer

The identified dialdehyde (**9**) leads us immediately to the initiating particle - a diradical intermediate - of the polymerization of the *p*-xylylene derivative (7a), providing us with strong evidence for the radical and self initiating character of the polymerization of *p*-quinodimethane derivatives leading to precursors for poly(*p*-phenylene vinylene) derivatives.

Carbon tetrabromide is generally known as an excellent transfer agent for radical polymerizations because of the weak C-Br bond (Ref. 10b). The addition of this agent results in a decrease of the molecular weight of the formed precursor polymer consistent with the radical character of the polymerization reaction. The polymerization yield did not change substantially under these circumstances.

Table I: Polymerization of premonomer (**6**a) in the presence of transfer agent Cbr$_4$

polymerisatie condities	$\overline{M_w}^{(a)}$	*opbrengst (%)*	$\overline{M_w}/\overline{M_n}$
standaard polymerisatie	663 000	25	2.9
+ 0.5 eq. (t.a.v. monomeer) CBr$_4$	296 000	30	2.2

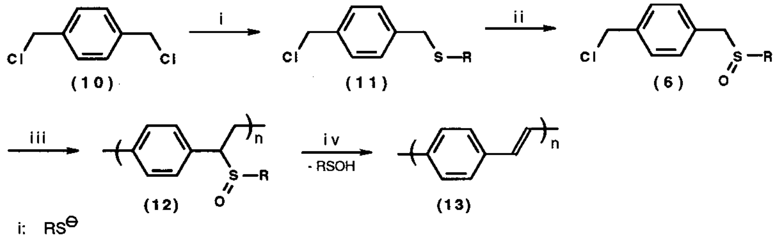
(a) determined against polystyrene standards in DMF at 1 ml/min (70°C).

One of the advantages of our route, is the possibility to vary the polarizer as well as the leaving group independently in the premonomer. We will use this to examine the effect of the leaving group and polarizer on the overall reaction.

When the elimination of the leaving group is the rate limiting step of the studied polymerization reaction, we expect an increase in molecular weight or yield of the polymer varying the leaving group from chloride, bromide to iodide. According to experiment there was no correlation between the leaving group capacity and yield or molecular weight of the formed polymer. On the other hand, the change of the polarizer from a sulfinyl group into a sulfonyl group causes a strong increase (10 times) of the molecular weight of the polymer. These groups determine the acidity of the hydrogen atom that should be abstracted in the first step of the observed reaction. This points to a process in which the abstraction of the proton in the premonomer is the rate limiting step in the formation of the *p*-quinodimethane system (**3**) in our route.

II. FINE TUNING OF SOLUBILITY CHARACTERISTICS

An(other) advantage of the precursor route discussed here, is the possibility to tune the properties of the precursor polymers by simply altering the R-group of the polarizer. In this way it is possible to optimise the solubility characteristics for spin coating thin films. It is known that homogeneous films are very important for obtaining high efficiency for the final P-LED. Also the elimination temperature of the polarizer can be of great importance for the performance of the P-LED, since Papadimitrakopoulos has shown that oxidation of PPV-films can be a serious problem which has a dramatic effect on the efficiency of the system (Ref. 12). The R-group can be introduced during the monomer synthesis by nucleophilic substitution of a *p*-dichloroxylene derivative (**10**) with the corresponding thiolate anion (Fig. 4). In this way it is possible to synthesise a great variety of different monomers (**6**). Polymerization of these monomers gives rise to high molecular weight polymers (**12**).

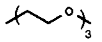


i: $RS^{\ominus}$
ii: H_2O_2
iii: NaOtBu
iv: Δ

Figure 4. General reaction conditions for monomer synthesis and polymerization

Table II shows the solubility characteristics of the precursor polymers obtained in this way. By changing the R-group it is possible to cover almost the whole spectrum of solvents, ranging from apolar solvents like toluene to polar solvents like alcohols and water.

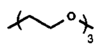
Table II: Dependence of solubility characteristics of the precursor polymer on R in the premonomer (**6**).

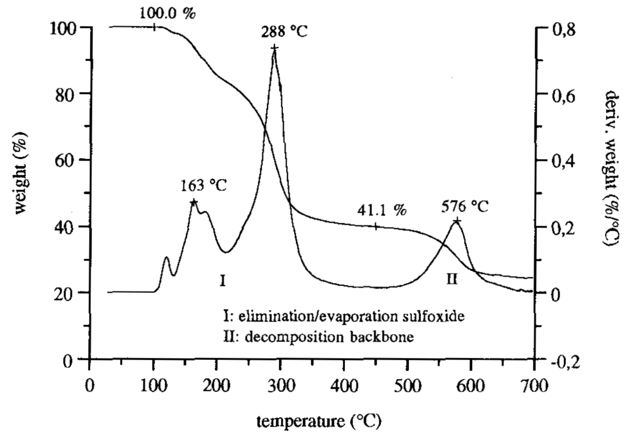
entry	R	$CHCl_3$	THF	Toluene	Alcohols	H_2O
6a	*n*-butyl	s	i	i	s	i
6b	*n*-octyl	s	s	s	s	i
6c	3-methylbutyl	s	s	i	s	i
6d	2-methylpropyl	s	s	i	s	i
6e	*t*-butyl	s	s	i	s	i
6f		s	s	i	s	s

s: soluble; i: insoluble

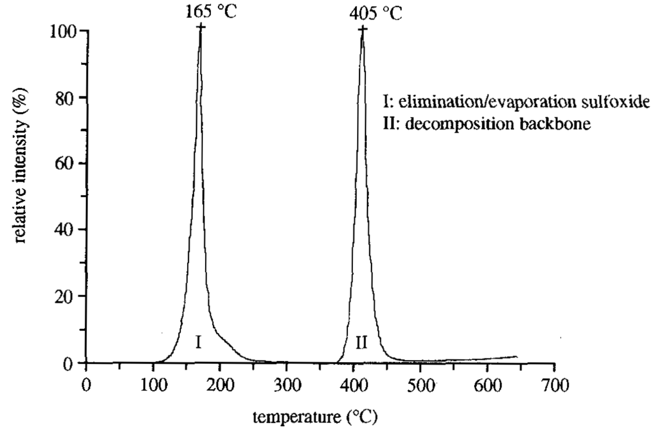
The thermal properties of the precursor polymers were investigated using Thermo Gravimetric Analysis (TGA) and Direct Insert Probe MS (DIP-MS). These are powerful techniques to follow the elimination reaction. Figure 5 shows the TGA-spectrum and DIP-MS

Table III: Elimination temperature of the sulfinyl group according to TGA and DIP-MS.

entry	R	TGA (°C)	DIP-MS (°C)
6a	*n*-butyl	165	163
6b	*n*-octyl	288	165
6c	3-methylbutyl	208	163
6d	2-methylpropyl	258	165
6e	*t*-butyl	153	159
6f		294	164



TGA-spectrum (20°C/min)



DIP-MS chromatogram (20°C/min)

Figure 5. TGA and DIP-MS of *n*-octyl precursor polymer **12b**

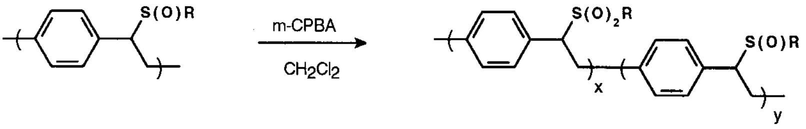
chromatogram of the *n*-octyl precursor polymer **12b**. The heating program for the TGA and DIP-MS was the same (20 °C/min). In both TGA and DIP-MS two degradation steps are observed. The first step is due to elimination of the sulfinyl group and the second step represents the decomposition of the polymer backbone. Table III depicts the elimination temperature of the different sulfinyl groups as determined in both techniques.

The large differences between the TGA and DIP-MS results (in most cases) come from the different atmospheres used. TGA is performed under a continuous flow of argon while DIP-MS is performed under high vacuum. In TGA the two processes, elimination and evaporation of the sulfinyl group, become more and more distinct processes as the R-group becomes larger and thereby more difficult to evaporate. Consequently the weight loss shifts to higher temperatures. In DIP-MS only one peak is observed because the eliminated sulfinyl group is instantaneously evaporated due to the high vacuum present in the instrument. As the elimination reaction is always performed under vacuum, one can expect that therefore elimination and evaporation of the polarizer will take place at about the same temperature (165 °C).

III. CHEMICAL MODIFICATIONS ON THE SULFINYL PRECURSOR

The micro structure of the conjugated polymer can have a strong influence on the final performance of the material in devices (Ref. 13). More specific, cristallinity and conjugation length have major impacts on the quantum efficiencies of the material (Ref. 14). Variations of the above described properties of the material can be realised by specific chemical modifications of the material. One modification is rendering the thermal eliminable groups into groups which cannot or less easily be eliminated. Thus defects in the conjugation are introduced when the material is treated under circumstances under which only sulfinyl groups eliminate and the defective groups reside. The number of defects will limit the average conjugation length and the conductivity of the material and determine the shift in UV-maxima. Furthermore a variation in photoluminescence efficiencies can be expected (Ref. 15).

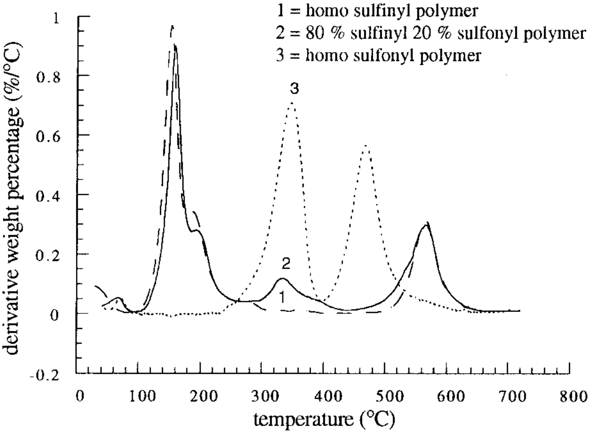
The sulfinyl group which is used as a thermally eliminable group has a wide variety of possibilities of chemical modification. The transformation of the sulfinyl group which is the most straightforward, is oxidation to a sulfonyl group. This can be achieved by a multitude of oxidants, e.g. *meta*chloroperbenzoic acid (Figure 6) (Ref. 16).



x, y = relative amounts of sulfinyl and sulfonyl groups in the modified polymer

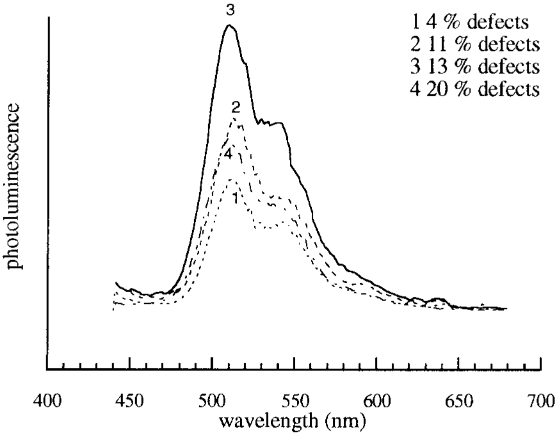
Figure 6. Partial oxidation of the precursor polymer **(12)**

This oxidation process of the precursor polymer has no effect on the average molecular weight as determined by GPC, as can be expected. TGA reveals that sulfonyl groups are more



Heating rate 10 °C/min, Argon Atmosphere

Figure 7. TGA of the sulfinyl, the partially and fully oxidized sulfinyl polymer.



Data are normalized for absorbance

Figure 8. Photoluminescence of partially oxidized precursor polymers after elimination

thermally resistant to elimination than the sulfinyl groups. So, the former groups will function as sp^3-defects in the conjugated system (Fig. 7). The first weight loss is due to the elimination of the sulfur functional groups. The second weight loss at 550 °C is due to the degradation of the conjugated system. The elimination circumstances have been investigated by IR analysis. The full elimination of sulfinyl groups and the remaining of the sulfonyl groups have been certified. The films which have been obtained after spin coating and elimination have been studied by UV and photoluminescence measurements, of which the latter is presented (Fig. 8.). The UV-results reveal an hypsochromic shift relative to the increasing amount of sulfonyl groups, pointing to a decreasing average conjugation length. The λ_{max} values from UV were used as excitation wavelength for the photoluminescence measurement. (copolymer 1 (4% defects): λ_{max}=428 nm, copolymer 2 (11 % defects): λ_{max}=424 nm, copolymer 3 (13 % defects): λ_{max}=424 nm, copolymer 4 (20 % defects): λ_{max}=415 nm)

IV. THE POLYMERIZATION OF MONOMERS WITH ENLARGED AROMATIC SYSTEMS

As stated above the ionic precursor route of Wessling and Zimmerman possesses some drawbacks (Ref. 11). One of the most important is the instability of the precursor polymers, which leads to gel formation and eventually insoluble precursor polymers, especially in the case of electron rich aromatic systems. Another drawback of this route is the fact that it is not possible to polymerise monomers with extended aromatic systems, like the 2,6-naphthalene and 4,4'-biphenyl derivative (Ref. 6). Using optimal leaving and polarizer groups in our polymerization route, may have the advantage that the base and solvent can be chosen in function of the monomer which must be polymerised. If it is to be expected that the change in resonance energy going from the aromatic premonomer to the non-aromatic *p*-quinodimethane

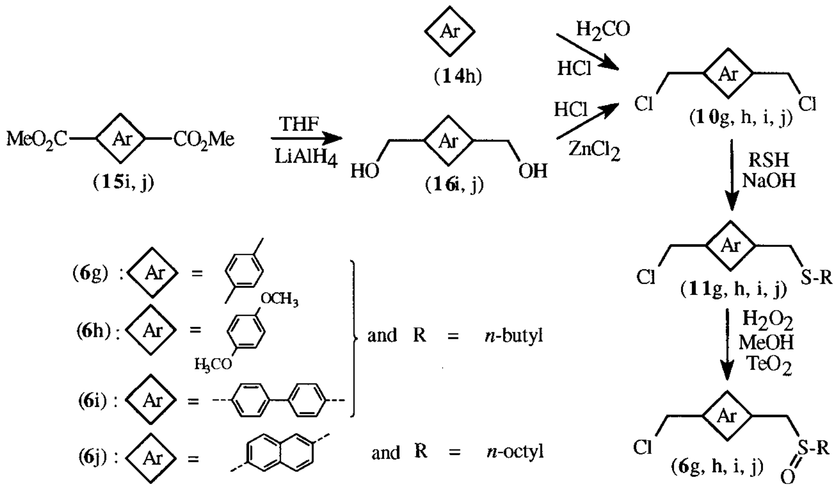


Figure 9. Procedures for the synthesis of the monomers (**6**g-j).

system becomes very large, it may still be possible to find a suitable base-solvent combination that makes the reaction feasible. The aim of this part of the work is to vary the aromatic core of the monomer and to find the base-solvent system most suited for the polymerization of the corresponding monomers. We will show that with our route it is possible to synthesise stable electron rich precursor polymers and high molecular weight precursor polymers with an extended aromatic system.

The synthesis of the monomers is displayed in figure 9. For the synthesis of the sulfide (**11g**) we start from (**10g**). It is formed by means of NaOH, butanethiol and a phase transfer catalyst, Aliquat 336, in H_2O and toluene (Ref. 17). The thioether is used without any purification and oxidized to the sulfinyl derivative (**6g**) with H_2O_2 and TeO_2 in methanol (Ref. 18). In order to obtain (**6h**) we first had to synthesise (**10h**). This is done via a chloromethylation of (**14h**) (Ref. 19). For the synthesis of (**6i**) and (**6j**), first the methyl esters (**15i**) and (**15j**) are reduced to the alcohol (**16i**) and (**16j**) with $LiAlH_4$ in dry THF (Ref. 20a). These alcohols are chlorinated in a mixture of HCl and $ZnCl_2$ (Ref 20b). The thioethers (**11i**) and (**11j**) and sulfinyl derivatives (**6i**) and (**6j**) are synthesised with the same procedure as used for (**6g**) and (**6h**).

Table IV: Polymerization conditions, molecular weights and yields obtained for the monomers (6g-j)

Monomer	Polymerization solvents	$\overline{M}_w(.10^5)$	$\overline{M}_w/\overline{M}_n$	Yield(%)
(**6g**)	MMF	6.2	2.9	25
	Form./THF	3.9	2.4	20
	NMP	1.9	1.9	55
	DMSO	2.4	1.9	70
(**6h**)	MMF	2.7	1.8	35
	NMP	0.9	1.7	30
(**6i**)	NMP	0.5	1.8	33
	DMSO/THF (50/50)	0.5	2.1	45
(**6j**)	MMF/CH_2Cl_2 (50/50)	2.0	1.9	5
	NMP	1.6	3.7	30
	DMSO/THF (60/40)	2.4	5.2	45

MMF: N-methylformamide; Form.: formamide; THF: tetrahydrofuran;
NMP: N-methylpyrrolidone; DMSO: dimethylsulphoxide

The monomers are polymerised in several solvents or, in the case of a low solubility of the used monomer, in some solvent mixtures under nitrogen atmosphere at room temperature. In all cases Na^+tBuO^- is used as a base. All the molecular weights of the precursor polymers are determined by means of GPC relatively to polystyrene standards in DMF.

In all cases high molecular weight polymers with a monomodal weight distribution are obtained, except for the polymerizations of (**6i**) and (**6j**) in NMP and DMSO/THF which yielded bimodal distributions. Even when the molecular weight distribution has a bimodal character, it is still possible to separate the high molecular weight fraction of the polymers from the monomers and low molecular weight fraction by precipitation in a mixture of ether and THF. The molecular weights and yields displayed in the table IV concern the high molecular weight fraction of the polymer. All the precursor polymers are soluble in chloroform, dichloromethane, NMP, DMF and MMF. The precursor polymers were characterised with FT-IR, ^{1}H-NMR and ^{13}C-NMR. The thermal elimination of the sulfinyl groups and the degradation of the conjugated polymers were examined with TGA. The elimination temperature, degradation temperature and theoretical and experimental weight loss after the elimination are shown in the table V.

Table V: Summarised results of the Thermal Gravimetric Analyses for polymers (**12**g-j).

Polymer	Elimination temp. (°C)	Amount elimination (%)		Degradation temp. (°C)
		Theoretical	Experimental	
(**12**g)	154	55.1	64.7	489
(**12**h)	159	60.5	68.4	438
(**12**i)	147	62.7	65.3	577
(**12**j)	290	48.5	53.5	569

The precursor polymers can be stored in a freezer in solid form for several months without any occurrence of elimination. The thermal conversion of the precursor to the conjugated polymer seems not complete according to TGA. Though, the FT-IR spectra show no residual sulfinyl signals (± 1050 cm^{-1}). Still some signals which can be attributed to the alkyl chains of the elimination products, e.g. disulfides and thiosulfonates (± 2950 - 2870 cm^{-1}), can be observed. The use of a high dynamic vacuum can possibly remedy this situation. The temperature difference between the elimination and degradation processes is certainly large enough to preclude any degradation during the thermal conversion.

CONCLUSION

A new precursor route for Poly(Arylene Vinylene) derivatives has been presented. In this way non-ionic precursor polymers were obtained which show an enhanced thermal stability and are soluble in organic solvents. This enables a thorough structural characterization and the study of the mechanism. It was shown that a self initiating, free radical polymerization mechanism is at hand. Furthermore it was demonstrated that this route leads to possibilities to tune solubility characteristics and to introduce defects in the polymer backbone. Also the scope for this new route was explored. The first results indicate that the versatility exceeds that of the Wessling route, more specific stable electron rich precursor polymers were obtained and the synthesis of precursors for poly(*p*-biphenylene vinylene) and poly(2,6-

naphthylene vinylene) could be accomplished in our case, whereas it failed in the case of the Wessling route.

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