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Synthesis of high molecular weight poly(4,4′-bisphenylene vinylene) and poly(2,6-naphthalene vinylene) via a non-ionic precursor route

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In previous work a new non-ionic precursor route has been developed. This new route makes it possible to polymerise monomers which possess enlarged aromatic systems. High molecular weight poly(4,4′-bisphenylene vinylene) (**7a**) and poly(2,6-naphthalene vinylene) (**7b**) were synthesised. The synthesis of the monomers, the precursor polymer and the conjugated polymers is discussed together with their characterisation. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(arylene vinylene)s; synthesis; characterisation)

Introduction

Precursor routes for the generation of conjugated polymers 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 which has been shown to be very versatile is the route introduced by Wessling and Zimmerman in the late 1960s[1–3]. This route was investigated thoroughly by Lenz *et al.* in the 1980s[4]. Their precursor polymers can lead after thermal conversion to conjugated polymers, of which the most well known is poly(*p*-phenylene vinylene) (PPV). These polymers have good mechanical properties, high thermal stability, large conductivities, in some cases a strong anisotropy and they have even shown great promise for the development of polymeric light emitting diodes (P-LEDs)[5,6]. Still there are some drawbacks, which are inherent to this route, e.g. the instability of the precursor polymer, which can lead to gel formation[7]. These problems have been circumvented by Yamada *et al.* by substitution of the sulfonium groups in the precursor by alkoxy ether groups[8]. Another limitation documented in the literature is the observation that monomers which possess enlarged aromatic systems, e.g. 4,4′-bisphenylene or 2,6-naphthalene, show no tendency to polymerise under the circumstances used in general for the Wessling precursor route[7]. 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 polymerisation behaviour of *p*-quinodimethane systems, of which other examples can be found well before the 1960s[9].

In our work we have tried to define the prerequisites of such polymerisation routes. For this purpose we have introduced a scheme in which a clear distinction is made between the three steps of the process. First the actual monomer, the *p*-quinodimethane system, is formed *in situ*. Then, in the second step the polymerisation takes place, which in our view can be described as a self-initiating radical chain polymerisation[10]. The third step implies the conversion to the fully conjugated system. The monomer in this route possesses a leaving group and a polariser which differs from the former. The polariser stabilises the anion formed in the acid–base equilibrium and ensures head to tail polymerisation. The leaving group is necessary for the 1,6-elimination, forming the quinoid structure which polymerises.

This route has the advantage that the polariser, leaving group, base and solvent can be chosen as a function of the monomer which must be polymerised. In our group it was shown that an *n*-butylsulfinyl group as polariser and a chloride as leaving group leads to stable and soluble precursor polymer[11]. Even the electron rich precursor polymers poly{[2,5-dimethyl-1,4-phenylene]-[1-(*n*-butylsulfinyl)ethylene]} and poly{[2,5-dimethoxy-1,4-phenylene]-[1-(*n*-butylsulfinyl)ethylene]} are stable and easy to handle. They can be stored in their solid state during several months in a refrigerator with no or minor occurrence of elimination and spin-coated or cast into films and easily thermally converted to the conjugated polymer[12]. In this paper it is shown that it is also possible to polymerise the 2,6-naphthalene and 4,4′-bisphenylene derivative to high molecular weight polymers using the same polymerisation route.

Results and discussion

The monomers used for the polymerisation, 4-chloromethyl-4′-[(*n*-butylsulfinyl)methyl]bis-phenyl (**5a**) and 2-chloromethyl-6-[(*n*-octylsulfinyl)methyl]naphthalene (**5b**), are synthesised by a similar procedure. In the first step the methyl esters (**1**) are reduced to the corresponding alcohol (**2**) with $LiAlH_4$ in dry tetrahydrofuran (THF)[13]. These alcohols are chlorinated by means of HCl and $ZnCl_2$[14]. The thioethers (**4**) are synthesised with *n*-alkylthiol, NaOH and a phase transfer reagent, Aliquat 336, in water and toluene[15]. The thioethers are used without any purification for the oxidation to the sulfoxide (**5**) with H_2O_2 and TeO_2 in methanol[16] (*Figure 1*).

In our laboratory the experience exists that the polymerisation of chloromethyl-4-[(*n*-butyl-sulfinyl)methyl]-benzene is successful in both aprotic polar solvents, like

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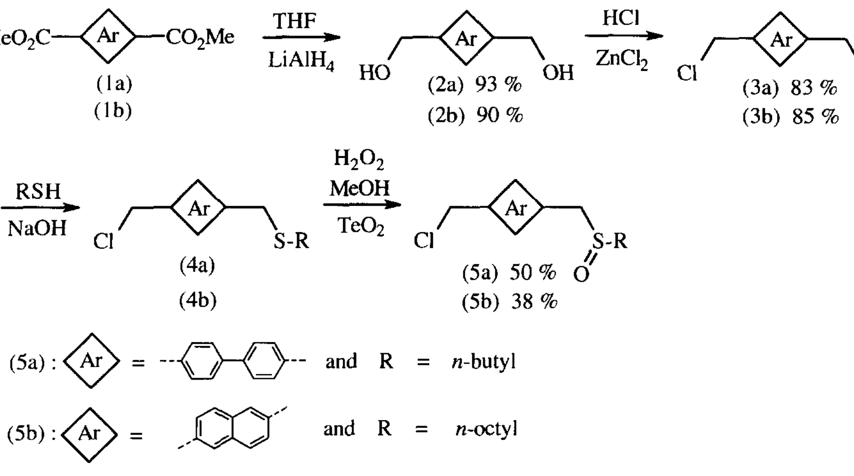

Figure 1 Synthesis of the monomers and reaction yields

N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO), and protic polar solvents, such as N-methylformamide (MMF)[10,11]. In the cases of monomer (**5a**) and (**5b**) the polymerisations are performed in four different solvents or solvent mixtures (MMF, MMF/CH_2Cl_2, NMP and DMSO/THF) under an inert atmosphere. Because of the low solubility of the monomers in MMF and DMSO, CH_2Cl_2 and THF are added. The monomers are dissolved in the chosen solvent or solvent mixture and 1.3 equivalents of sodium *tert*-butoxide are added as a base. In the case of the polymerisation of (**5b**) in DMSO/THF only one equivalent of base is used. The polymerisation is allowed to proceed for 1 h, then the reaction mixture is poured into water and neutralised with a 0.1 M HCl solution (aq.). The suspension is extracted with chloroform and the organic layer is concentrated on a rotary evaporator after which the polymer is precipitated in a mixture of diethylether and THF, filtered and dried in vacuo (*Figure 2*).

We first tried to polymerise (**5a**) and (**5b**) in MMF and a mixture of MMF and CH_2Cl_2 (50/50). No polymer was formed in the case of (**5a**). On the other hand, when the polymerisation of (**5b**) was performed in MMF/CH_2Cl_2, high molecular weight polymer was obtained with a monomodal molecular weight distribution, though the yield was low. When the polymerisations of (**5a**) and (**5b**) were carried out in NMP, high molecular weight material with a bimodal molecular weight distribution was formed. In both polymerisations the yield was moderate. It was possible to separate the high molecular weight polymer fraction, the low molecular weight fraction and the monomer by means of two precipitations in a mixture of 90/10 ether and THF and 70/30 ether and THF in that order. The polymerisation was also performed in a mixture of DMSO and THF. Under this condition high molecular weight material was obtained as well. The molecular weight distribution was bimodal and even here the high and low molecular weight fraction of the polymer and the monomer were separated. The origin of the bimodal molecular weight distributions is under current investigation. At this time we assume that the bimodal distribution is caused by two polymerisation mechanisms occurring at the same time when aprotic polar solvents are used. It seems that a radical chain mechanism and an anionic polymerisation are responsible for the high and low molecular weight fraction respectively. The results of this work will be published elsewhere. The molecular weights and yields displayed in *Table 1* concern both the high and low molecular weight parts of the polymers.

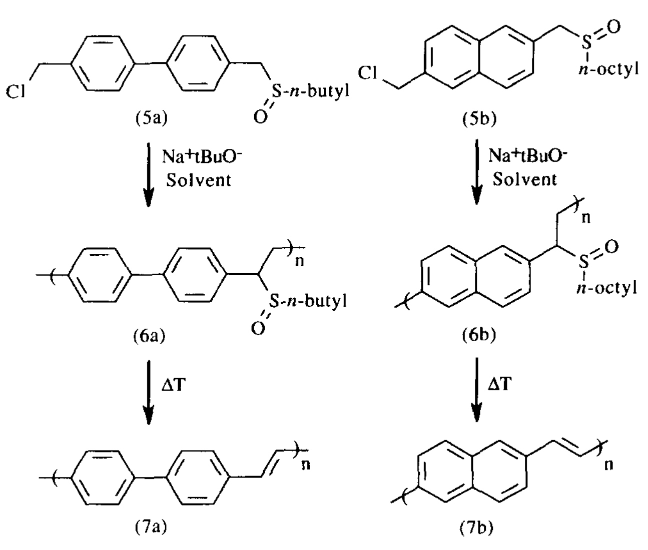

Figure 2 Polymerisation and conversion to the conjugated polymer

These polymers are completely soluble in CH_2Cl_2, $CHCl_3$, NMP, MMF and DMF. All precursor polymers are colourless or almost colourless. The slight colouring when the reaction is carried out in the aprotic solvents (NMP and DMSO/THF) is caused by the excess base which is used, and can be avoided by using only one equivalent of base. All ^{1}H and ^{13}C n.m.r. data are consistent with the proposed precursor polymer structure.

The thermal elimination of the sulfoxide groups and the degradation of the conjugated polymers are examined with thermal gravimetric analysis (t.g.a.). The analyses are performed under a flow of nitrogen, the rate of heating was 20°C/min. The precursor polymer derived from (**5a**) exhibits a first region of weight loss from 120 to 290°C. The weight loss of 35% approaches the theoretical 37% of the elimination of the sulfenic acid. A second weight loss is observed at 530°C which corresponds to the degradation of the conjugated polymer. The elimination of the sulfenic acid of the naphthyl derivative (**6b**) takes place in a temperature range from 135 to 315°C. After this loss of mass 53% of the initial weight of the sample is reached, while 46% is the

Table 1 Polymerisation results

Polymer	Solvent	High molecular weight part			Low molecular weight part		
		$\bar{M}_w$ ($\times 10^4$)^a	D^a	Yield (%)	$\bar{M}_w$ ($\times 10^4$)^a	D^a	Yield (%)
(6a)	MMF	0	0	0	0	0	0
	MMF/CH_2Cl_2 (50/50)	0	0	0	0	0	0
	NMP	5.6	1.8	33	0.4	1.1	9
	DMSO/THF (50/50)	4.9	2.1	45	0.9	1.6	10
(6b)	MMF/CH_2Cl_2 (50/50)	20.5	1.9	5	0	0	0
	NMP	16.5	3.7	30	0.9	1.2	5
	DMSO/THF (60/40)	24.5	5.2	45	1.0	1.3	8

^{a} Molecular weights and dispersities according to GPC relative to polystyrene standards and with DMF as eluent

theoretical value. The conjugated polymer (**7b**) is found to be stable up to 540°C, after which degradation occurs (*Figure 3*).

Solutions of the precursor polymers (**6a**) and (**6b**) were applied to a KBr pellet and subjected in vacuo to 200°C during 1.5 h and 220°C during 2 h respectively. *FT*i.r. spectra of (**7a**) and (**7b**) show that the S=O absorption at 1042 (**7a**) and 1033 cm^{-1} (**7b**) disappears completely while the vinylene vibrations at 956 (**7b**) and 967 cm^{-1} (**7a**) are clearly visible. In the spectra we also observe peaks at 1702 (**7a**) and 1705 cm^{-1} (**7b**) which points to some oxidation leading to a carbonyl stretch. The three bands at 2923–2853 and 2957–2870 cm^{-1} probably arise from $-CH_2-$ and $-CH_3$ vibrations of some residual elimination products. Thus, although the elimination of the sulfoxy groups is complete, some of the reaction products remain in the conjugated polymer matrix. This can explain the difference between the theoretical and experimental weight after the elimination in the t.g.a. When we reduced the film thickness of the polymer on the KBr pellet, the relative amount of residual elimination products strongly diminished.

The precursor polymers (**6a**) and (**6b**) were spin-coated on a quartz substrate and converted to the final conjugated polymers under the same circumstances as mentioned earlier. The u.v.–vis spectra of these films are shown in *Figure 4*. The absorption maximum of the greenish polymer (**7a**) (386 nm) is blue shifted relative to poly(*p*-phenylene vinylene) (PPV) (424 nm). The maxima of the absorption bands of the naphthyl derivative (426 nm) and PPV are almost the same. The edges of the absorption band of the napthyl and bisphenyl derivative are situated at 2.51 eV and 2.68 eV respectively (PPV: 2.35 eV) (*Figure 4*).

The photoluminescence measurements were carried out on the same samples as used for the u.v.–vis measurements. The normalised results are illustrated in *Figure 5*. PPV synthesised according to our route emits yellow light with a maximum at 544 nm and a shoulder at 516 nm. The photoluminescence spectrum of polymer (**7b**) is blue shifted compared to PPV. It has a maximum at 518 nm and emits greenish light. The bisphenyl derivative (**7a**) shows emission maxima at 467 and 497 nm which corresponds with green–blue light (*Figure 5*).

Conclusions

The results show that it is possible to polymerise monomers with an enlarged aromatic system, like 4-chloromethyl-4'-[(*n*-butylsulfinyl)methyl]bisphenyl (**5a**)

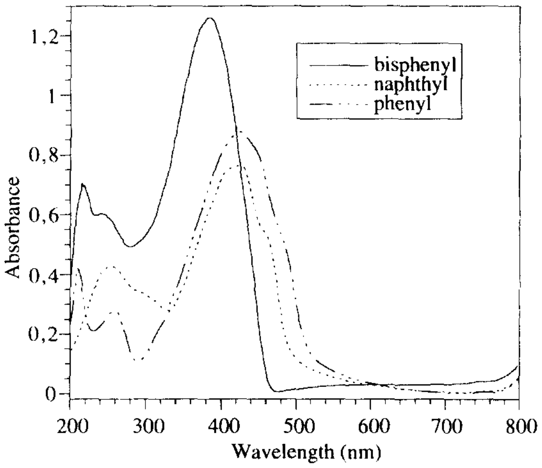

Figure 4 U.v.–vis measurements on films of polymer (**7a**) and (**7b**)

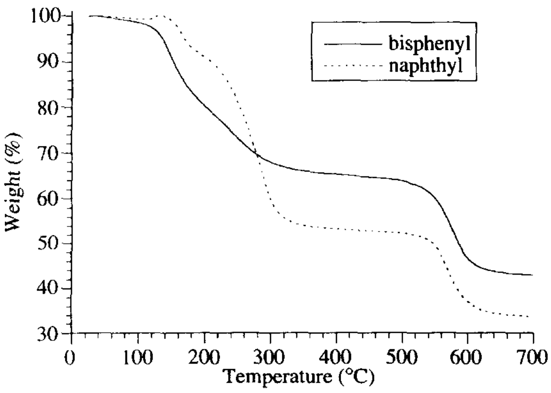

Figure 3 T.g.a. of the precursor polymers

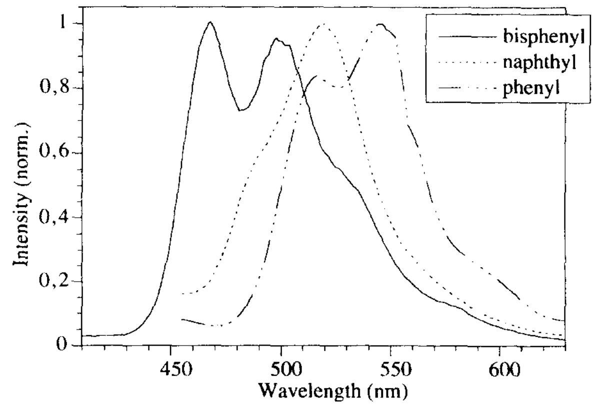

Figure 5 Photoluminescence spectra of the conjugated polymers

and 2-chloromethyl-6-[(*n*-octylsulfinyl)methyl]naphthalene (**5b**), to high molecular weight with the non-ionic precursor route described. This is possible due to the fact that, with this generalised route, we are able to tune the reaction circumstances according to the monomer which must be polymerised. The precursor polymers (**6a**) and (**6b**) are stable in solid form and soluble in several organic solvents. It is possible to make films of these precursor polymers which can easily be thermally converted to their conjugated form, poly(4,4′-bisphenylene vinylene) (**7a**) and poly(2,6-naphthalene vinylene) (**7b**). The fluorescence of these conjugated polymers shifts to the blue relative to PPV.

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