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Electrochemical synthesis of poly(*p*-xylylenes) (PPXs) and poly(*p*-phenylenevinylenes) (PPVs) and the study of xylylene (quinodimethane) intermediates; an underrated approach

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The electrosynthesis of poly(*p*-xylylenes) (PPXs) and poly(*p*-phenylenevinylenes) (PPVs) by the direct and mediated cathodic reduction of (halomethyl)arenes is reviewed and, where appropriate, comparisons made with more conventional chemical routes. Attention is drawn to the advantages of mild (non-thermal) conditions and to the consequent toleration of a wide range of substituents in the (halomethyl)arene precursors. Copolymers are obtained by co-electrolyses and aprotic and aqueous conditions may be used. Several polymers that are inaccessible by the Wessling and related routes may be prepared electrochemically. The properties, including lifetimes, of the key quinodimethane (xylylene) intermediates have been examined by cyclic voltammetry and the results are consistent with a radical-chain mechanism for polymerisation, initiated by electrogenerated radical-anion. The physical properties of electrochemically derived polymers are comparable *re* molecular weight and photoelectrical properties to those prepared chemically.

Introduction

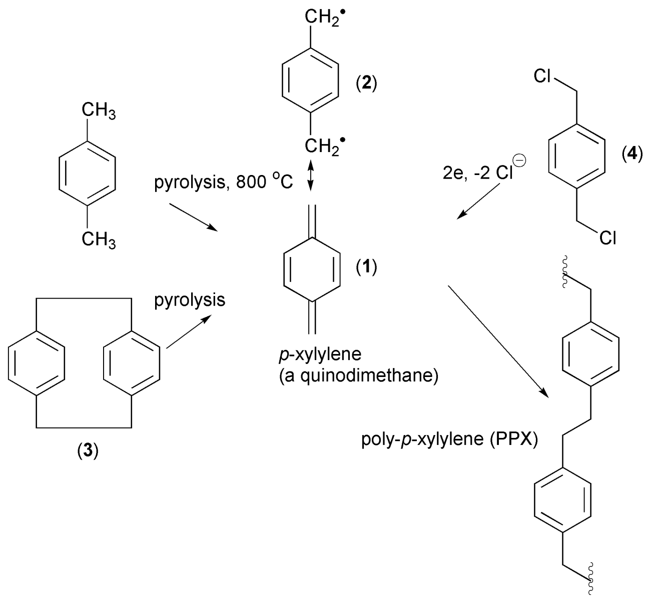
Electrochemical methods have recently made a substantial contribution to the synthesis of a variety of poly(*p*-xylylenes) (PPXs) and poly(*p*-phenylenevinylenes) (PPVs) and to the study of the key xylylene (quinodimethane) intermediates. Those committed to conventional approaches to polymer synthesis have largely ignored these advances, even[1,2] in recent literature, although organic electrochemistry is not conceptually or practically difficult. Recent reviews and books are available[3–5] for introductions to the subject. In this article we attempt to redress the balance and to demonstrate the versatility of the electrochemical method and those situations where it offers advantage. For the study of mechanism and characterisation of reactive intermediates electroanalytical methods are often the method of choice.

Electrosynthesis has, of course, been widely used for the preparation of polypyrroles, polythiophenes, polyanilines and related polymers, usually as intractable films. And electroanalytical methods, *e.g.* cyclic voltammetry, are used[6] in continuing attempts to determine the still uncertain mechanism(s) of such oxidative couplings. Here we exclude such systems and have chosen to restrict discussion to PPXs and PPVs and in particular to consider electrochemical and some more conventional chemical methods that are believed to involve quinodimethane intermediates.

1. Quinodimethanes

The parent *p*-quinodimethane (**1**, *p*-xylylene, Scheme 1) was first described[7,8] by Szwarc as a product of the pyrolysis at 800 °C of *p*-xylene. He concluded that it was stable in the gas phase but that on condensation on a surface it polymerised rapidly to give a white film insoluble in common organic solvents, although a small soluble fraction turned out to be *p*-cyclophane (**3**, Scheme 1), which can also be converted into **1** pyrolytically. Errede[9] developed fast flow pyrolysis and condensed the resulting xylylene in hexane at −78 °C. Furthermore he was able to estimate the concentration of the intermediate by iodometric titration and follow its decay as it polymerised; at −78 °C the $t_{1/2}$ was *ca.* 21 h. Several substituted *p*-xylylenes (and consequently polymers) were formed by pyrolysis and co-pyrolysis[10,11] gave co-polymers. At −78 °C polymerisation of **1** can be initiated by momentary contact with a warm surface and it then proceeds as 1st order with respect to the monomer;[12] the growing chain is not terminated by chain transfer with solvent (hexane or toluene) or by reaction with oxygen, although chain transfer did take place with thiophenol.[10]

Coulson and his co-workers[13] calculated that the quinonoid form of **1** was more stable than the alternative triplet diradical



Scheme 1

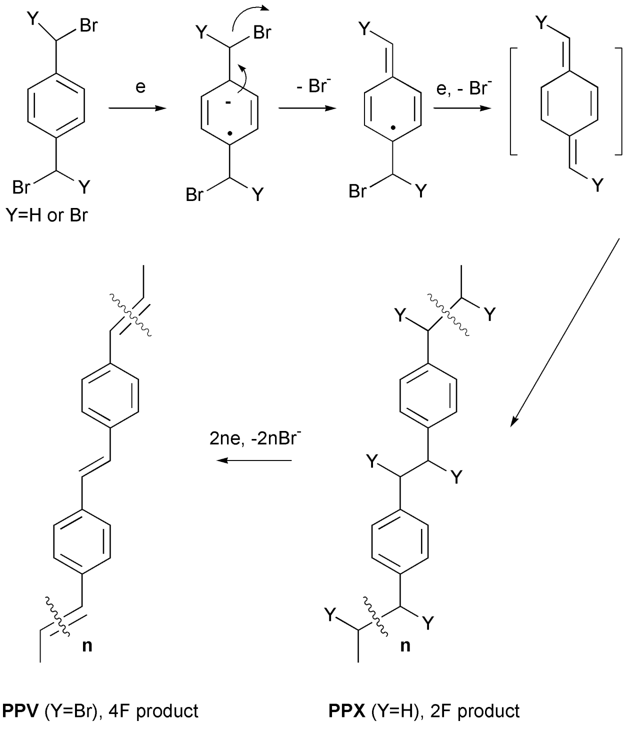
2 (Scheme 1) by *ca.* 50 kJ mol^{-1} and this conclusion was confirmed when Williams and his co-workers[14] measured the ^{1}H NMR spectrum of a condensed sample in d$_8$-THF at -80 °C. The methylenic and ring proton signals were sharp, *i.e.* clearly diamagnetic, with distinct singlets occurring at 5.1 and 6.5 ppm respectively.

The first electrochemical preparations of PPXs followed Gilch's attempt[15] reductively to cleave chlorine from hexachloro-*p*-xylene using zinc and acetic acid. Instead of the expected α,α,α,α′,α′-pentachloro-*p*-xylene he obtained a high yield of the PPX, poly(tetrachloro-*p*-xylylene). Arguing correctly that electron transfer was probably involved he found that controlled potential reduction of α,α′-dihalo-*p*-xylenes, at a mercury cathode, was effective in the preparation of several PPX derivatives; yields from bromides were significantly higher than from chlorides. Covitz followed up this work with a detailed polarographic, slow scan cyclic voltammetric and coulometric study[16] in DMF solution that confirmed the versatility and efficiency of the method and that both *p*- and *o*-PPXs could be formed, probably *via* xylylene intermediates. It was also established that, as for the pyrolysis reactions, a minor by-product was *p*-cyclophane (**3**, Scheme 1). Nishihara and his coworkers[17] discovered that reduction of α,α,α′,α′-tetrabromo-*p*-xylene at indium tin oxide (ITO) gave PPV albeit as a thin film suitable only for optical studies.

2. Recent explorations of the electrosynthesis of PPXs and PPVs

2.1 Direct cathodic reduction—general aspects

The electrochemical generation of xylylenes and the PPX and PPV polymers derived from them is conveniently described in Scheme 2. Much of the evidence for this will be described later, but at this stage it is worth noting that reduction is carried out[18,19] in a divided cell at a mercury pool cathode, in aprotic solvent (*e.g.* DMF) and at the first reduction potential, as determined by cyclic voltammetry. Coulometry shows that the 1,4-bis(halomethyl)arenes consume 2 F and the 1,4-bis(dihalomethyl)arenes consume 4 F. The use of a stirred mercury pool cathode allows reduction to go to completion because insoluble polymer is constantly removed from the surface and does not insulate the electrode surface and hence stop reaction. It is convenient to explore the scope of the method using controlled potential reduction at mercury in aprotic solvent, usually on a 0.5–2.0 g scale. However, at least for the preparation of the soluble poly(2,5-dimethoxy-*p*-phenylenevinylene) scale up to a 100 g or more scale is possible using[20] an undivided flow cell with constant current at a lead cathode and aqueous DMF.



Scheme 2

In contrast to pyrolytic and chemical routes, electrochemical methods are non-thermal and providing that substituents are not themselves easily reducible a wide range of functionality can be tolerated,[18,19,21–23] probably functions that would not survive the high temperatures or strongly basic conditions associated with alternative chemical routes. Furthermore, the flux of reactive intermediates can be controlled by control of concentration, current, and potential. This offers the possibility of control of molecular weight and it is often possible to produce[18,19,22,23] substantial proportions of organo-soluble PPXs and PPVs. And co-electrolysis[18,19,21] of different 1,4-bis(halomethyl)arenes results in random co-polymers.

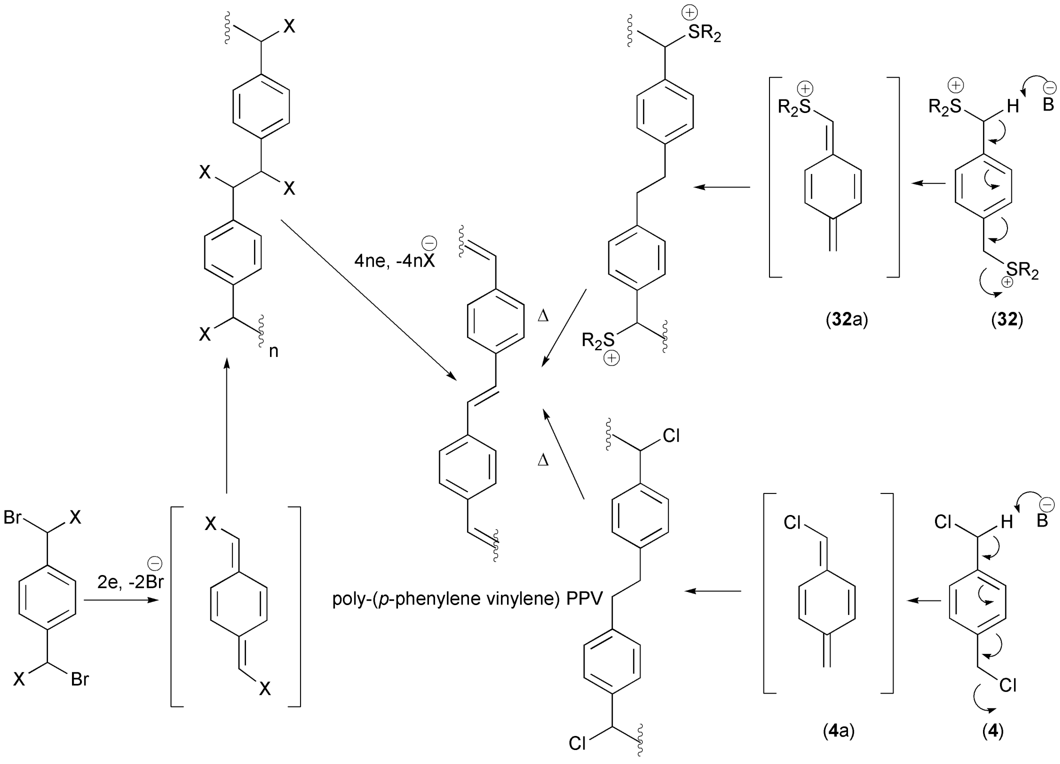
Similarities between the cathodic route and the commonly used Wessling[24] and Gilch[25] methods are illustrated in Scheme 3. Although mechanistic uncertainties remain, the common intermediacy of xylylenes is well established; much less certain is the mechanism(s) whereby the xylylenes polymerise. A more comprehensive comparison with the most relevant chemical routes (Scheme 3) will be made later.

2.2 Poly(xylylenes)

Many of the bis(halomethyl)arene precursors used for conversion into the corresponding poly(xylylenes) are shown as formulae **5**–**34**. Table 1 lists the conditions used and the yields.[18,21–23] When referring to a PPX polymer derived from one of the precursors we will designate it with the suffix **P**, hence the polymer derived from **26** is **26P**. For completeness some examples of 1,2-bis(bromomethyl)arenes have been included (**15**–**18**); strictly the polymers derived from these precursors are poly(*o*-xylylenes, *o*-PXs).

The precursor polymers involved in chemical routes to PPVs are PPXs (Scheme 3) and efficient cathodic conversion of a salt of 1,4-bis(dimethylsulfoniomethyl)benzene, **32**, into PPX has been achieved.[26,24] Unfortunately the cleavage of both sulfonium functions precludes further conversion into PPV. In a seemingly related example it is claimed[27] that the corresponding 1,4-bis(triphenylphosphoniomethyl)benzene, **33**, was converted cathodically into PPV as a film at an ITO cathode. The electrochemical conditions are not correctly described—the cathode potential and the coulometry are not recorded. However, it is highly unlikely that the reaction proceeds *via* reductive 1,4-elimination of triphenylphosphine, which would lead to *p*-xylylene and hence PPX. More likely is reaction at the surface with electrogenerated base to produce the ylide that would eliminate 1 equivalent of triphenylphosphine to give the xylylene (**34**) that would proceed to give PPV by analogy with Scheme 3. There is excellent precedent[28,29] for cathodic conversions into phosphonium ylides either directly or *via* electrogenerated bases.

The electrochemical method can be made to work in aqueous media,[21] probably because the intermediate quinodimethanes are neutral and "radical-like" and therefore relatively unaffected by a change from aprotic to protic media. The polymers so produced are water-soluble and can be isolated in the free acid forms (acidic functions are SO$_3$H and CO$_2$H) by treatment with ion exchange resins. These products may be re-dissolved in water. Furthermore, metal-containing polymers, with high metal content, were obtained by precipitation from aqueous solution with iron, copper or barium salts.



Scheme 3

Co-polymers may be readily synthesised by co-electrolysis of different precursors and some examples are given in Table 1, which includes an example of a water-soluble PPX.

An interesting analogy with *p*-xylylene formation is the probable intermediacy of a 1,4-bis-ketene in the electroreduction of terephthaloyl chloride.[30] In this reaction intractable cross-linked polymers (polyterephthaloylenes) are formed because the initial polymer is so easily further reduced whereby it undergoes further uncontrolled reaction with the starting material (terephthaloyl chloride).

2.3 Poly(*p*-phenylenevinylenes)

The precursors that have successfully been electroreduced to the corresponding PPVs are given as formulae **35–57** and Table 2 gives yields and reaction conditions.

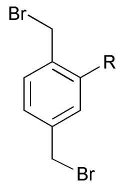
As for the PPXs (Table 1) the range of functionality tolerated is significant, as is the ready formation of random copolymers by co-electrolysis of equivalent amounts of different substrates, and copolymers of PPVs with PPXs have also been achieved. The characterisation of the polymers and copolymers will be discussed later. There is much scope for further experimentation here, as so far studies have been restricted to copolymers with equal amounts of the constituents.

Another feature is the formation of PPVs derived from the biphenyl derivatives **50–54** and from the terphenyl derivative **55**. This is in contrast to the confident claim[1] that the Wessling route fails in such cases because the intermediate xylylenes are relatively unstable as they cannot achieve planarity. The precursor **49** leads to an *ortho*-coupled PPV despite the suggestion that such polymers probably cannot be made chemically. The formation of the polymers **56P** and **57P** might be expected to be vulnerable to steric hindrance but have been

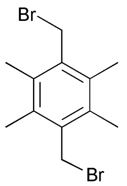
Table 1 Electrosynthesised[a] poly(xylylene) polymers and copolymers

Precursor	$-E_{red}$/V	Yield of poly(xylylenes) (%)	Precursor	$-E_{red}$/V	Yield of poly(xylylenes) (%)
5	1.3	90	**21**	1.2	54[22]
6[b]	1.5	78	**22**	1.9	72
7[b]	1.5	72	**23**	1.4	45
8[b]	1.5	90	**24**	1.2	70
9[c]	1.8	70	**25**[b]	1.5	74
10	0.85	80	**26**	1.1	72
11	1.4	40	**27**[e]	1.6	76
12	1.4	40	**28**	1.9	35
13	1.5	76	**29a**	1.3[f]	Quant.[g]
14a[d]	1.7	60	**30**	1.5	93[23]
15	1.4	33	**31**	1.9	54[23]
16	1.8	42	**5** + **15**	1.3	64[h]
17[b]	1.5	56	**5** + **13**	1.5	99[h]
18	1.4	5	**6** + **10**	1.5	57[h,i]
19	1.1, 1.5	26,66[22]	**29a** + **29b**	1.3[f]	Quant.[h,g]
20	1.3	84[22]			

[a] Divided cell, Hg pool cathode, DMF–Et_4NBr (0.1 M), electrolysis to *ca.* 2 F, V *vs.* Ag/AgBr, ref. 18 unless otherwise indicated. [b] Only DMF-soluble formed. [c] DMF-soluble and insoluble fractions, *ca.* 1 : 3. [d] DMF-soluble and insoluble fractions *ca.* 1 : 8. [e] DMF-soluble and insoluble fractions *ca.* 1 : 1.6. [f] V *vs.* SCE. [g] Hygroscopic, therefore water content uncertain. [h] Copolymer formed by co-electrolysis of equivalent amounts of precursors. [i] DMF-soluble and insoluble fractions *ca.* 1 : 0.63.



5 R=H; **6** R=OCOCH$_3$
7 R=OCOC$_7$H$_{15}$
8 R=OCOPh
9 R=OMe



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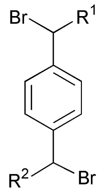
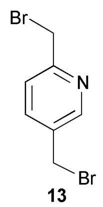


11 R^1=Me, R^2=H
12 R^1=R^2=Me



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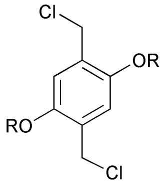
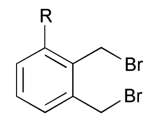
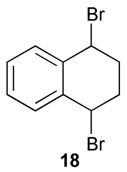


14a R=Me
14b R=H



15 R=H; **16** R=OMe
17 R=O.COCH$_3$



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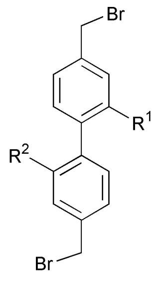
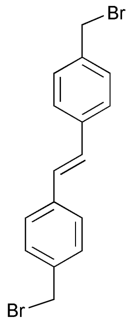


19 R^1=R^2 = H
20 R^1=R^2 = OMe
21 R^1=R^2 = NO$_2$
22 R^1=H, R^2=OC$_{10}$H$_{21}$
23 R^1=H, R^2=SO$_2$C$_{10}$H$_{21}$



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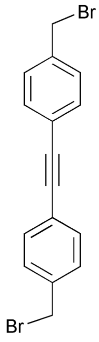

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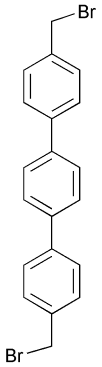

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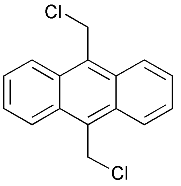

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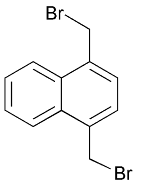

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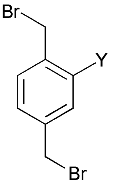
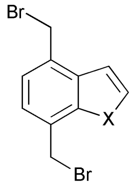
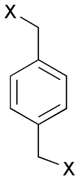


29a, Y = SO$_3$H
29b, Y = CO$_2$H



30 X = O
31 X = S



32 X = Me$_2$S$^+$
33 X = Ph$_3$P$^+$

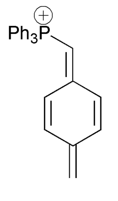


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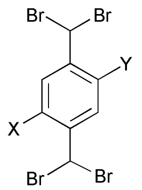
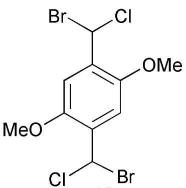
Table 2 Electrosynthesised[a] poly(phenylenevinylene) polymers (PPVs) and copolymers

Precursor	$-E_{red}$/V	Yield of poly(phenylenevinylene)[b] (%)	Precursor	$-E_{red}$/V	Yield of poly(phenylenevinylene)[b] (%)
35	1.25	80	**53**	1.8	77[33]
36	1.03	95	**54**	1.3	64[34]
37	1.60	89	**55**	2.4	52[34]
38	1.03	37	**56**	1.65	74[31]
39	1.70	82	**57**[b]	1.52	92[31]
40	1.30[c]	Quant.[d,21]			
41	1.30[c]	Quant.[d,21]	**36** + **5**	1.2	65[e]
42	1.3	90[35]	**35** + **5**	1.3	50[e]
43	1.4	95[35]	**36** + **46**	1.0	82[e]
44	2.0	85[35]	**36** + **47**	1.3	70[e]
45	1.80	82	**40** + **41**	1.5[c]	Quant.[e]
46	0.70	92			
47	1.30	62			
48	1.00	72			
49	1.00	37			
50	1.60	85[36]			
51	1.80	60[36]			
52	1.5	77[36]			

[a] Divided cell, Hg pool cathode, DMF–Et$_4$NBr (0.1 M), electrolysis to *ca.* 4 F, V *vs.* Ag/AgBr, ref. 19 unless otherwise indicated. [b] Insoluble and DMF-soluble product. [c] V *vs.* SCE. [d] Hygroscopic, therefore water content uncertain. [e] Copolymer formed by co-electrolysis of equivalent amounts of precursors.



35 X=Y=H; **36** X=H, Y=OCOMe
37 X=H, Y=OMe; **38** X=H, Y=CO$_2$Me
39 X=Y=OMe; **40** X=H, Y=SO$_3$H
41 X=H, Y=CO$_2$H; **42** X=H, Y=OCOC$_{11}$H$_{23}$
43 X=H, Y=SCOC$_{11}$H$_{23}$; **44** X=H, Y=OC$_{10}$H$_{21}$



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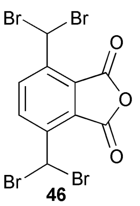

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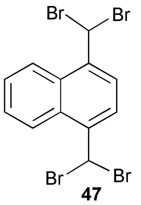

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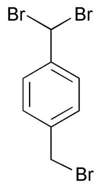

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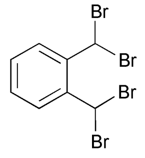

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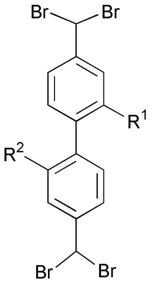
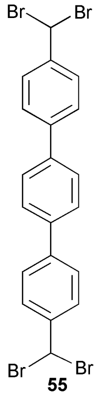


50 R^1 = R^2 = H
51 R^1 = H, R^2 = OMe
52 R^1 = H, R^2 = NO$_2$
53 R^1=H, R^2=OC$_{10}$H$_{21}$
54 R^1=H, R^2=SO$_2$C$_{10}$H$_{21}$



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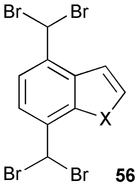
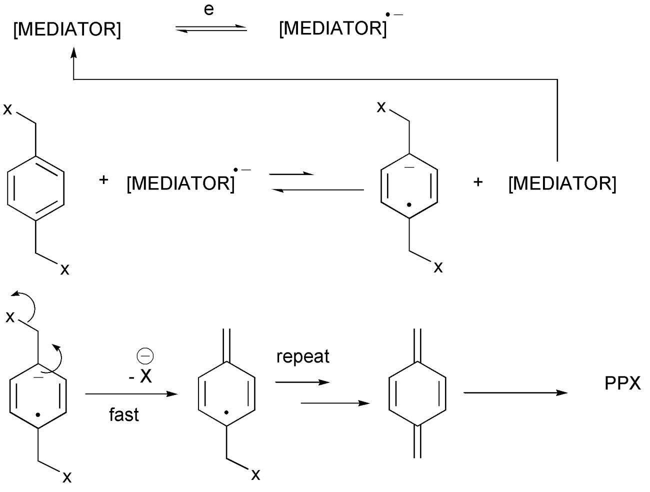


56 X = O
57 X = S

made both electrochemically[31] and *via* the sulfonium route.[32] In the light of the success of the electrosynthetic method it is more likely that intermediates react slowly and that electrogeneration is more effective because close to the cathode surface high concentrations are involved, both of xylylenes and of potential initiators (radical-anions?)

By analogy with the results for PPX formation (Table 1) water-soluble PPVs are accessible by the electrochemical route as are copolymers, including co-polymers of PPV and PPX units.

The data in Tables 1 and 2 are restricted to citing total yields of PPXs and PPVs. In most cases fractions are obtained that are either soluble or insoluble in DMF. This aids the characterisation and measurement of the properties of several of the polymers and co-polymers (see later section).



Scheme 4

2.4 Indirect electrolysis

Electrochemistry can sometimes be employed in the generation and regeneration of reagents (mediators), in these cases reducing agents. Because less than stoichiometric amounts of electrogenerated reagent are used, and in a sealed reaction system, the method is environmentally friendly. In certain circumstances the mediators are formed reversibly and regenerated rapidly because of a fast irreversible reaction with the target substrate. This is likely to be the case for reduction of bis(halomethyl)arenes because loss of halide anion from benzylic radical-anions is very fast and sometimes held to be concerted with electron transfer (dissociative electron transfer). In these circumstances the peak current of the mediator is greatly enhanced in the presence of substrate to give a diagnostic "catalytic current". The theory of such "redox catalysis" is well established[37,38] and redox catalysis is likely in our systems by analogy with the reductive elimination of vicinal dihalides.[39,40] The route for mediated electrogeneration of xylylenes (quinodimethanes) is given in Scheme 4. The E^0 value for the mediator is less cathodic than for the substrate reduction and typically ΔE_{red} should be <0.5 V.

This approach works well for synthesis of PPXs and PPVs by the mediated cleavage of 1,2- and 1,4-bis(bromomethyl)arenes and the corresponding tetrabromo derivatives. Significantly, however, it offers a solution to an inconvenience of the electrosynthetic method. In most cases bromomethyl derivatives have been used; their reduction potentials are less cathodic than are those of the corresponding chlorides and in most cases reduction of the chlorides gives cathodic hydrogenolysis, *e.g. p*-xylene is obtained by reduction of 1,4-bis(chloromethyl)benzene. However, in generating xylylenes for characterisation and for reactivity studies it was discovered that certain relatively stable radical-anions and low-valence transition metal complexes or compounds are effective redox catalysts for reduction of bis(halomethyl)- or bis(dihalomethyl)-arenes in general, including the chlorides (see Scheme 4). The operation of this mechanism is readily confirmed by cyclic voltammetry that shows the characteristic "catalytic current"—an example[41] using Ni(salen) as mediator is given in Fig. 1. Examples of the mediated electrosynthesis of PPXs

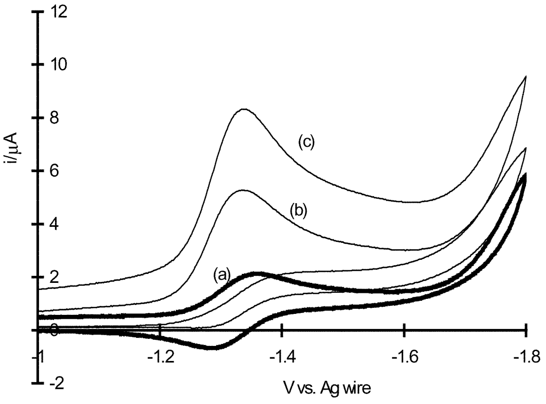


Fig. 1 Cyclic voltammetric evidence for redox catalysis of reductive cleavage of compound **64**; Hg/Pt cathode, DMF–Et_4NBr (0.1 M), 0.1 V s^{-1}; (a) Ni(salen), 0.9 mM, (b) as for (a) + **64** 1.1 mM, (c) as for (a) + **64** 2.8 mM.

and PPVs from bis(chloromethyl)benzenes are given in Table 3. These results are drawn from recently published examples.[41–43] Apart from the successful applications of mediated electrolysis for the cathodic cleavage of the 1,4-derivatives it should be noted that polymers are also formed by electrolysis of 1,2-(halomethyl)arenes. For convenience these are denoted as *o*-PX (*o*-polyxylylene) polymers. The Wessling route does not apparently[1] form polymers from the *o*-substituted precursors.

In many cases, therefore, PPXs and PPVs can be made from chloride precursors. Also convenient is the use of bis(bromochloromethyl)arenes, such as **45**—they are readily prepared by free-radical bromination of the chloromethyl derivatives that in turn can be made by chloromethylation of arenes.

3.0 Characterisation and reactivity of quinodimethane (xylylene) intermediates

3.1 Cyclic voltammetry

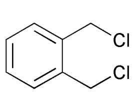
Fortuitously many quinodimethanes are less easily reduced than the bis(bromomethyl)arenes from which they are formed. This allows observation of the reduction peaks of quinodimethanes by single sweep cyclic voltammetry and, as the scan rates may be varied over several orders of magnitude, the timescale of these experiments can be varied.

Consequently an idea of reactivity may be gleaned and

Table 3 PPXs and PPVs *via* mediated electrolysis[a] of bis(chloromethyl)arenes

Precursor	Mediator	$-E^0$ (mediator)/V[b]	$-E_{red}$ (precursor)/V	$-E_{red}$ (electrolysis)/V[c]	Yield (%) of PPX or PPV	Reference
4	Ni(II)Cl_2dppe	0.88, 1.41	2.11	1.9	PPX (80)	43
	Ni(II)Cl_2dppp	0.57, 1.47	2.11	2.0	PPX (98)	43
	Ni(salen)	1.67	2.11	1.4	PPX (50)	41
	62	1.76	2.11	1.45	PPX (75)	41
14a	Ni(salen)	1.67	2.03	1.40	PPX (83)	41
	62	1.76	2.03	1.50	PPX (75)	41
59	Ni(salen)	1.67	1.90	1.40	PPX (50)	41
58	Ni(II)Cl_2dppe	0.88, 1.41	2.09	1.8	**63** (20)	43
	61	1.61	2.11	1.6	*o*-PX (42)	42
	Dimethyl terephthalate	1.61	2.11	1.6	*o*-PX (42)	42
	Perylene	1.63	2.11	1.6	*o*-PX (43)	42
45	$CrCl_3{\cdot}6H_2O$ + anthranilic acid	1.30	1.70	1.30	PPV (76)	41

[a] Hg pool cathode, divided cell, DMF–Bu_4NBF_4 (0.1 M), mediator usually at 10 mol% and reduced exhaustively prior to introduction of substrate and subsequent continued reduction. [b] V *vs.* SCE, Hg/Pt cathode, CV at 0.2 V s^{-1}. [c] V *vs.* Ag wire.



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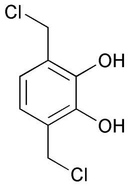

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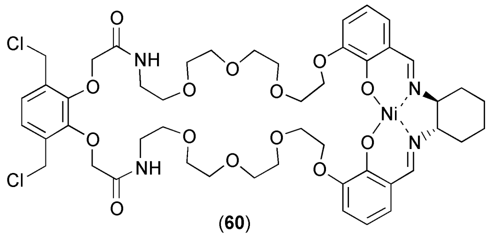

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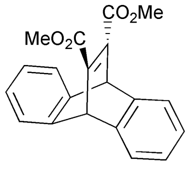

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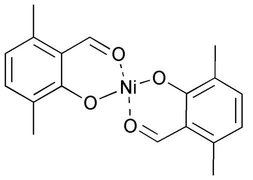

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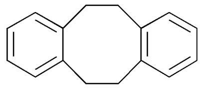

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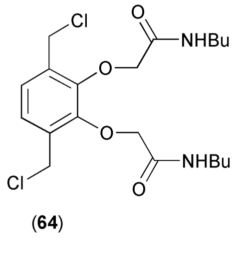

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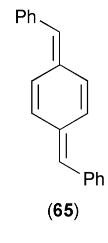


(65)

Table 4 Reduction potentials[a] of starting materials and of the quinodimethanes formed[44,42]

Substrate	$-E_{\mathrm{red}}(1)/\mathrm{V}^b$	$-E_{\mathrm{p}}(\mathrm{QDM})/\mathrm{V}$
5	1.27	1.93[b]/1.935[c] (**1**)
4	2.11	1.93[b] (**1**)
66 (see text)	0.80	1.495 (**65**) [E^0]
67 (see text)	1.96	1.495 (**65**) [E^0]
14a	2.05	1.923[b]
19	1.35	1.992[b]
15	1.22	1.74[b]

[a]Formal potentials with reference to SCE measured by cyclic voltammetry at 1–200 V s^{-1} in 2 mM solutions DMF –Bu_4NPF_6 (0.1 M) at an Hg/Pt electrode, at room temperature. [b]Peak potential at 1 V s^{-1}. [c]E^0 at −15 °C, Au-cathode, 160 V s^{-1}.

standard redox potentials (E^0) measured and the relationship between the E^0 values and structure informs about such factors as the planarity of the quinodimethanes. A selection of reduction potential values is given in Table 4.

Fig. 2 shows the reduction pattern observed[44] for a relatively long-lived quinodimethane **65**, derived from **66** and for the parent *p*-quinodimethane (**1**, *p*-xylylene) derived from **5**. For Fig. 2a and 2b, the second peak corresponds to reduction of the quinodimethane and at 100 V s^{-1} reduction of **1** can be observed but it is irreversible whereas that of **65** is at least quasi-reversible. This implies that the radical-anion of **1** reacts quickly and it is likely that this is by direct addition to another molecule of **1**, leading to rapid polymerisation. In contrast the radical-anion of **65** is relatively long-lived which is consistent with stabilisation through delocalisation of spin and charge over the 1,4-phenyl groups. Proof that the peak seen in Fig. 2b relates to reduction of **65**, and an interesting manifestation of redox catalysis, is seen in the cyclic voltammetry of the dichloride **67** (Fig. 2c and 2d). A single scan over the full potential range (Fig. 2c) shows an irreversible reduction peak that is less cathodic than that for the quinodimethane **65**. However, continuous cycling into the foot of that reduction wave causes a reversible couple to develop at the E^0 value found for **65**, *i.e.* the same quinodimethane (**65**) is generated from both the bromo and the chloro precursors. This is because small amounts of radical-anion generated at the foot of the wave catalyse the reduction of the precursor at a potential at which **65** is not further reduced.

The irreversibility of the reduction of **1** may be outrun at 160 V s^{-1} and −15 °C (Fig. 3) and a quasi-reversible peak is seen[44] under these conditions. This implies that polymerisation in the electrochemical method can proceed by initiation by radical-anions and that for the parent quinodimethane (**1**) it is on the millisecond timescale at cyclic voltammetric concentrations (a few millimolar).

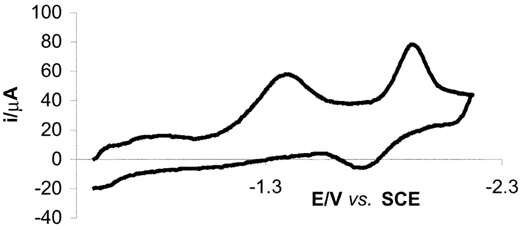


Fig. 3 Cyclic voltammetry of 5 (1,4-bis(bromomethyl)benzene) [2 mM in DMF–Bu_4NPF_6 (0.1 M), Au cathode], −15 °C, 160 V s^{-1}.

3.2 The mechanism of polymerisation of quinodimethanes

The mechanism whereby quinodimethanes (xylylenes) polymerise thermally has been much studied and the routes most considered are summarised in Scheme 5. Szwarc and Errede first speculated[11] that the process began by dimerisation of *p*-xylylene (known to exist in the quinonoid form) to give, reversibly, a diradical (**68**) that in turn would lead in the critical step to a tetramer in which the central -CH_2CH_2- bond would approach normal bond strength; at this point a relatively stable diradical initiator would be present. In the diradical **68** for instance the central -CH_2CH_2- bond will be weak because of the facile reversible reaction to the xylylene. It was proposed that in the gas phase reversibility to the xylylene would predominate, accounting for the relatively long lifetime of xylylenes in the gas phase, but that at the higher concentrations in the condensed phase irreversible formation of the tetramer initiator would be plausible.

Solution phase studies of *p*-xylylene (**1**) reactivity depended on the introduction[9] of a technique whereby the intermediate formed in the gas phase by pyrolysis, *e.g.* of *p*-xylene (Scheme 1), was condensed in heptane or toluene at −78 °C. At this temperature *p*-xylylene has $t_{1/2}$ of 22 hours whereas at −36 °C $t_{1/2}$ = 22 minutes. Polymerisation was initiated by brief contact with a warm surface and the first-order decay of *p*-xylylene followed[12] by iodometric titration; the E_{act} was found to be 36 kJ mol^{-1}. Despite the assumption of radical chain propagation no chain transfer was observed with common reagents except for mercaptans. There was also no interaction with atmospheric oxygen yet preparative experiments showed[45] that *p*-xylylene in solution will co-polymerise with an excess of oxygen.

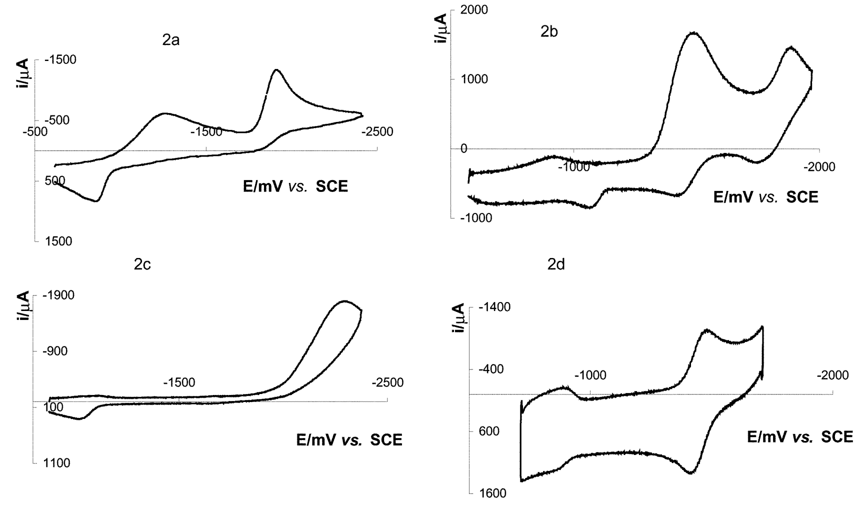
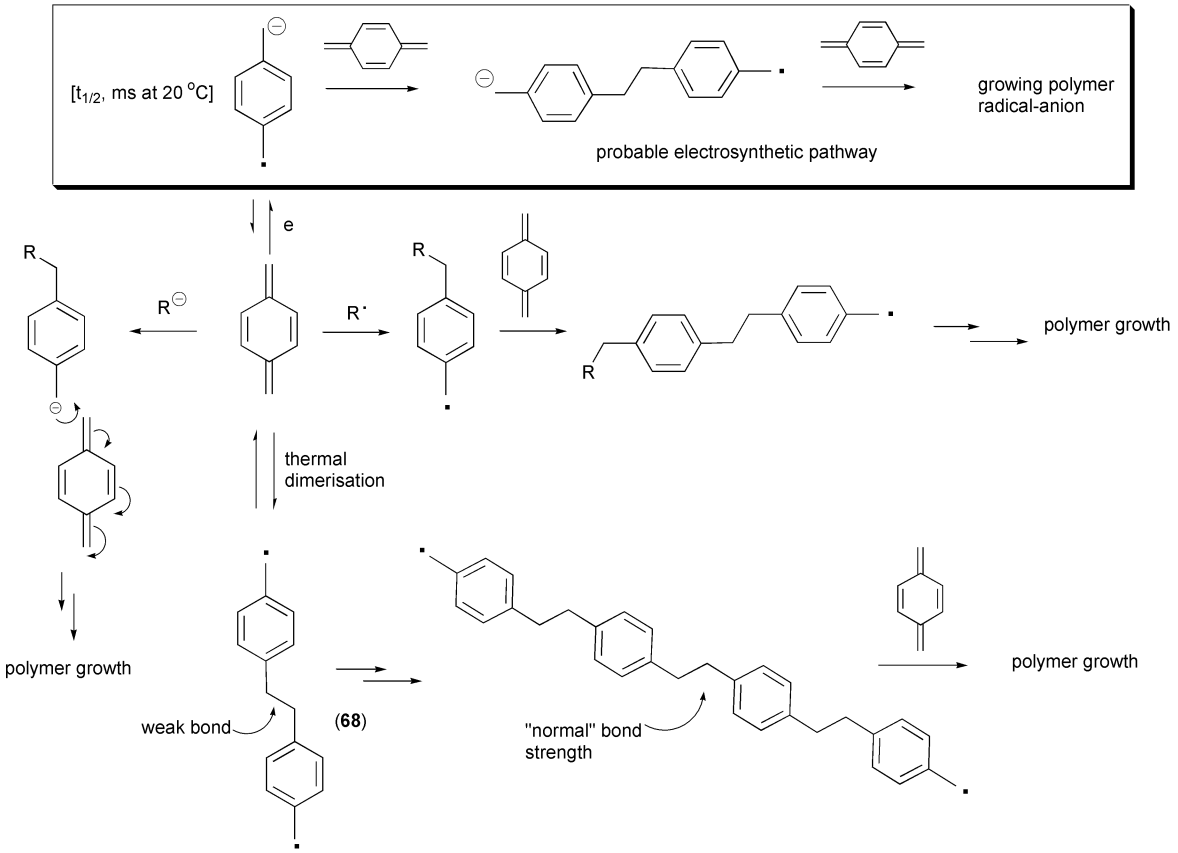
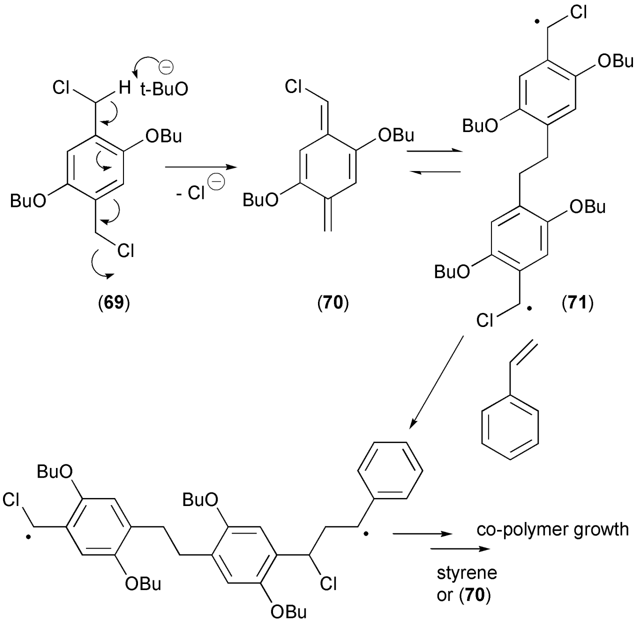


Fig. 2 Cyclic voltammetry of 1,4-bis(halomethyl)arenes [2 mM in DMF–Bu_4NPF_6 (0.1M), Hg/Pt cathode]. 2a; 1,4-bis(bromomethyl)benzene, (**5**), 100 V s^{-1}; 2b; 1,4-bis(α-bromobenzyl)benzene (**66**), 100 V s^{-1}; 2c; 1,4-bis(α-chlorobenzyl)benzene (**67**), 100 V s^{-1}; 2d; 1,4-bis(α-chlorobenzyl)-benzene, 100 V s^{-1}, continuous cycling.



Scheme 5

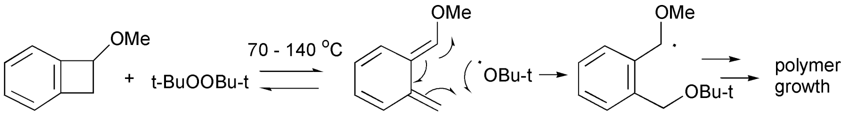
The quinodimethane intermediate in the Wessling route (**32a**, Scheme 3) has a characteristic UV absorption[24] at *ca.* 310 nm that greatly assists study of this reaction. This feature has been used[46] to establish that sulfonium substituted xylylenes are indeed the key intermediates in the Wessling route, but unfortunately no useful kinetic information could be obtained. Initially, because the Wessling route employs strongly basic conditions, anionic polymerisation was proposed,[47] a view reinforced by the apparent lack of inhibition by radical-trapping reagents such as TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl radical). However, a later study[48] showed that radical traps, including oxygen and TEMPO, had a profound effect on the molecular weights of the PPX products and on the rates of decay of sulfonium xylylene intermediates, as followed by UV spectroscopy.



Scheme 6

More support for the radical pathway comes from the results of co-polymerisation experiments[49] involving styrene and a base generated quinodimethane, **70** in Scheme 6. Essentially, the intermediate **70**, formed by elimination from the corresponding bis(chloromethyl)arene **69**, reacts with added styrene at 50 °C to give copolymers under conditions where styrene alone does not polymerise. Scheme 6 shows a plausible explanation in terms of initiation by the diradical **71**, although the route would also accommodate initiation by a tetramer diradical as proposed by Szwarc and Errede.[11]

Contrary to reports in earlier reviews[1] *o*-quinodimethanes do polymerise and this has been recorded for both base-induced reaction[50] and for electroreduction.[42] Strangely therefore the "first" polymerisations of *o*-quinodimethanes have been claimed[51] as the result of experiments on the thermal isomerisation of benzocyclobutenes. Benzocyclobutenes are also claimed to be the most convenient precursors of quinodimethanes despite scant consideration of any other method. However, the experiments[52] outlined in Scheme 7 are germane to the mechanistic discussion and powerful support



Scheme 7

for the radical initiation pathway. The scheme reports the proposal[52] of Endo *et al.* and it is significant that in the absence of the peroxide initiator only oligomers and dimers are formed from the benzocyclobutene pyrolysis. A recent report[42] is devoted entirely to the electrochemical generation of *o*-quinodimethanes and a study of their reactivity.

In conclusion, there is compelling evidence for the radical initiation and propagation of the polymerisation of quinodimethanes produced by the chemical routes. For the polymerisation of electrogenerated quinodimethanes it is probable that initiation involves radical-anions acting as radicals rather than anions (Scheme 5). These would certainly be formed during preparative electrolysis.

4.0 Properties and characterisation of PPXs and PPVs

4.1 Infrared spectroscopy

IR spectroscopy has been widely used for the characterisation of both PPX and especially for PPV polymers.[53] As expected, the main characteristic bands are present, regardless of the preparative route, although particular bands can differ and may be helpful to indicate the degree of conversion and some structural features, as for instance, the ν_{C-S} band at $\sim$630 cm^{-1} or the ν_{C-Br} band at $\sim$615 cm^{-1} for, respectively, the conversion into PPV *via* a sulfonium, soluble, precursor or *via* cathodic reduction. For PPVs from both routes, the band at $\sim$960 cm^{-1} indicates a *trans* configuration of the vinylene function, whereas polymers obtained *via* the Wittig reaction also show absorption at $\sim$700 cm^{-1} due to the presence of *cis* double bonds. PPV obtained electrochemically may present bands at $\sim$1478, 1397, 1167 and 1107 cm^{-1}, which indicate a certain degree of doping, probably by the supporting electrolyte.[54] Inadequate handling precautions of thin PPV films exposed to air may result in the formation of carbonyl groups on the chain (oxidative degradation), and the corresponding $\nu_{C=O}$ band appears at 1690 cm^{-1} which is characteristic of a conjugated ketone group. For both PPV and PPX, the δ_{C-H} out-of-plane bending absorptions for substituted benzene rings are useful not only for discerning *ortho*-, *meta*-, and *para*-polymers, but also for determining if cross-linking occurred during preparation. This is not normally the case for electrosynthesised PPVs/PPXs due to the inherently mild conditions employed. Other vibrational modes useful in confirming structure have been observed[55] by Raman spectroscopy of an electrochemically deposited PPV film, although this was not, as the authors presume, the first electrosynthesis of PPV!

4.2 Ultraviolet–visible spectroscopy

UV–Vis absorption spectra of electrochemically prepared PPVs show a similar pattern[31,36] to the spectrum of thermally obtained unsubstituted PPV.[53] Thus, they present a well-defined low-energy maximum at approximately 3.3 eV (π–π^* delocalised), a second weaker feature at $\sim$5 eV (delocalised π to localised π^* and localised π to delocalised π^*), and a strongly increasing absorption above 5 eV (π–π^* within a single phenylene ring). The observed energy gaps depend on the electronic nature of the substituents, as well as on the chain structural features. Thus, a red shift is observed with electron-donating side-groups in contrast to a blue shift with electron-withdrawing ones. Poly(biphenylenevinylene)s also display a blue shift, probably reflecting the degree of non-coplanarity of the phenylene rings caused by steric hindrance between the 2,2′-substituents.[36] There is a good agreement between these energy gap values and those determined by cyclic voltammetry (described later).

4.3 NMR spectroscopy

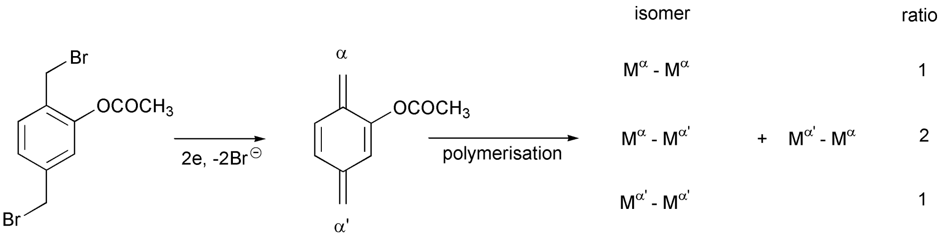
^{1}H and ^{13}C NMR spectroscopy has been widely used for the characterisation of soluble PPVs and PPXs. Insoluble polymers have been examined[18,19] by solid-state ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR, which can also provide some information about the crystallinity and morphology of polymer films.[56,57]

NMR analyses of electrosynthesised PPX[18] and PPV[19] gave good evidence that there is no significant branching or cross-linking. PPXs bearing side-groups (*e.g.* **6P**) presented three broad singlets for the CH$_2$ hydrogens, which integrate in the ratio 1 : 2 : 1. This is evidence of a statistical coupling of the quinodimethane involved (**M**), giving rise to α,α, α,α' and $\alpha'\alpha'$ linkages (Scheme 8), which suggests a low energy of activation with an early transition state and no discrimination between the different pathways. This result is consistent with radical chain propagation (see section 2.2).

4.4 Direct pyrolysis mass spectrometry (DPMS)

The linear structures of PPXs have been nicely established[58] by high-resolution mass spectrometric examination of fragments (up to six monomer units) formed by *in situ* pyrolysis. In PPXs the central -CH$_2$CH$_2$- linkage is relatively weak and in a regular linear PPX all such benzylic bonds in the polymer are equally likely to break and an equal probability of survival (p). This leads to a simple relationship whereby the intensity of a peak in the mass spectrum for the n-mer fragment (i_n) is related to the quantity ($n - 1$) by $\ln i_n = (n - 1)\ln p + C$, where C is a constant. The observation of good linear plots of $\ln i_n$ *vs.* ($n - 1$) confirmed the validity of the assumption, and hence gave compelling evidence for regular linear PPX structures. Because the central bond in PPVs is stronger they are less easily pyrolysed although DPMS did allow the observation[19] of fragments composed of up to three monomer units.

The DPMS method is especially powerful for showing that copolymers formed by co-electrolysis are true copolymers and not intimate physical mixtures of the homopolymers. This approach depends on the observation of fragments containing both monomer units; these are easily distinguished in high resolution MS. The method works for PPX copolymers,[18] PPV copolymers[19] and copolymers formed from both PPX and PPV precursors.[19] In general it can be shown that the copolymers are formed by random combination.



6 **M** **6P**

Scheme 8

4.5 Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetry (TG) have been used to evaluate polymer thermal stability and softening points. Most of the electrochemically prepared PPXs[18,23] and PPVs[36,19] were found to be stable in air up to 150–400 °C, depending on the nature of the substituents, and their softening points are quite high. Above these temperatures, complete degradation takes place usually in two exothermic processes. In many cases, the weight loss of the first step corresponds roughly to the relative molecular weight of the substituent, suggesting that degradation starts by its loss. Kinetic investigation of the thermal degradation of **50P** was achieved from TG data[59] by the application of Ozawa's method,[60] in which the slope of plots of log heating rate *vs.* $1/T$ gives the activation energy (E_a) of the process, which for this polymer is 116 ± 4 kJ mol^{-1}. A remarkable fact is the amount of heat evolved by thermal decomposition of nitrated polymers (*e.g.* **21P**, **52P**) which was an order of magnitude higher than that observed for other substituted similar polymers.[36,22]

4.6 Cyclic voltammetry

Cyclic voltammetry experiments of thin PPV films deposited on polished metal electrodes (Au, Pt) showed well-defined reversible oxidation and reduction waves.[54,61] By pulsing the potential between the two waves, electrogenerated chemiluminescence is observed with the same emission as the photoluminescence spectrum and can be assigned to an excited state formed in an annihilation process between electrogenerated oxidised and reduced centres in the immobilized polymer film.

A value for the band gap, defined as the difference between onset potentials for reduction and oxidation, can be accurately deduced.[62] Thus, for instance, an electrogenerated PPV (**35P**) film on a Au electrode gave, by this method, an energy gap of 2.40 eV, which is in excellent agreement with the π–π* peak observed in the UV–Vis spectrum (2.39 eV) of the same polymer sample.[54] The ionisation potential (5.35 eV) could be estimated using the valence effective Hamiltonian (VEH) technique[63] and the electron affinity (2.95 eV) was considered as the difference between IP and E_g.

4.7 Electrical properties of PPVs

4.7.1 In the pristine form. Devices constructed from thin films of PPV (*e.g.* **50P**,[64] **57P**[65]) sandwiched between a low-work-function metal (for electron injection) and a high-work-function metal (for hole injection), Fig. 4, were examined for their current dependence on voltage, $I(V)$.

Different physical explanations were reported for the control of the current density in conjugated material films subjected to external voltages. Low charge carrier mobility materials commonly present a current dependence on voltage, $I(V)$, characteristic of transport limited by space-charge accumulation, as was observed for devices made of Au/**50P**/Al. In such cases, the current density (j) is expressed as[64]

$$j = \frac{9}{8}\varepsilon\mu\frac{V^2}{d^3}$$

where ε is the polymer relative permittivity, μ is the charge carrier mobility, V is the applied voltage and d is the film thickness. The low positive charge carrier mobility (μ) found for **50P**, 6×10^{-9} cm^2 V^{-1} s^{-1} (*cf.*[66] 2×10^{-6} cm^2 V^{-1} s^{-1} for PPV), as well as its absorption spectrum,[36] suggest that this polymer behaves in a similar way to PPP, with twists in the biphenylene units and the consequent weak π-conjugation among the rings strongly influencing the transport and optical properties.

Injection limited transport has also been observed (*e.g.* for Al/**57P**/x devices, x = Ga, Sn and Sb) due to the high potential barrier at metal/polymer interfaces and can be well described by the Fowler–Nordheim tunneling expression:[67]

$$I \propto F^2 \exp\left(\frac{-K}{F}\right)$$

where I is the current, F is the electric field strength and K depends on the barrier shape. Assuming a triangular barrier shape at the interface, K is given by[68]

$$K = \frac{8\pi\sqrt{2m*}\varphi^{3/2}}{3qh}$$

where φ is the barrier height, m^* is the charge carrier (electron or hole) effective mass, q is the magnitude of the electron charge and h is the Planck constant. Using these equations, the potential barrier height (φ) was calculated for several metal/polymer (**57P**) interfaces, and since $\varphi = \phi - \chi$ (see Fig. 4) the electron affinity of **57P** was determined as being 4.04 eV, which indicates a decrease in the LUMO level energy when compared with that of PPV ($\chi = 3.87$ eV).[69,70] This result is in good agreement with theoretical quantum chemical predictions[65] (a stabilisation between 0.2 and 0.4 eV, depending on the method). The electron affinity and the band gap (2.92 eV, from UV–Vis) of this polymer make it a promising candidate for the electron injection layer in multilayer devices.[32]

Devices involving blended conjugated polymers may present very unusual electrical properties. Thus, for instance,[71] Cr/**36P**–PMMA/Cu [PMMA = poly(methyl methacrylate)] presents rectifying character, but with a very large dependence of current density (J) on applied voltage (V), at forward bias

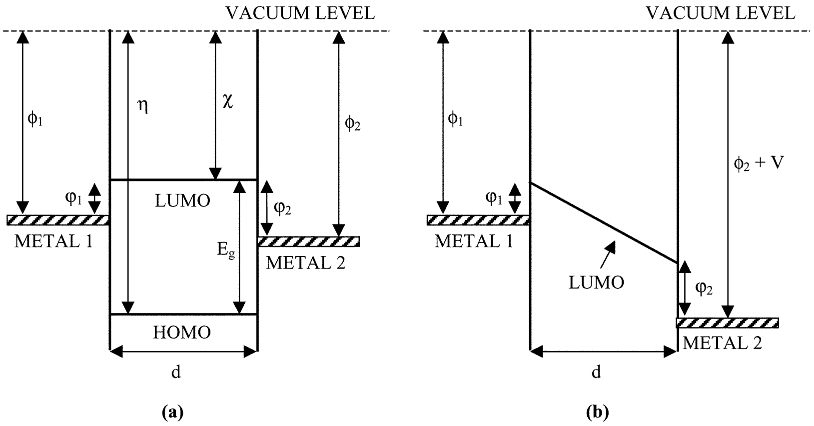


Fig. 4 Band structure of a metal/polymer/metal sandwich device: (a) flat band condition and (b) under applied voltage. ϕ, metal work-function; φ, potential barrier height at metal/polymer interface; η, ionisation potential; χ, electron affinity; E_g, energy gap; d, polymer film thickness; V, applied voltage.

Table 5 Average molar mass and degree of polymerization of some insoluble polymer fractions determined by elemental analysis

PPX	M_w	n	Ref.	PPV	M_w	n	Ref.
9P	3700	26	18	**50P**	3350	17	36
19P	5750	31	22	**51P**	6275	25	36
20P	5200	21	22	**52P**	6200	22	36
21P	7200	26	22				

Table 6 Weight average molecular mass (M_w), number average relative molecular mass (M_n), polydispersity index (M_w/M_n) and degree of polymerization (n) of some soluble polymers determined by GPC

PPX	M_w	M_n	M_w/M_n	n	Ref.
22P	132 000	43 300	3.0	376	33
23P	25000	1950	13	63	33
25P	1459	1139	1.3	6	18
6P	37 933	5861	6.5	36	18
14bP	22×10^6	1.3×10^6	17	9000	41
29aP	6000	4000	1.5	30	21
(**29a** + **29b**)**P** copolymer	8760	6260	1.4	50	21
PPV					
42P	4300	1100	3.9	14	35
53P	53 500	7100	7.5	154	33
54P	3600	950	3.8	9	33
40P	2.3×10^5	1.15×10^5	2.0	1153	21
41P	1.15×10^5	7.2×10^4	1.6	826	21
(**40** + **41**)**P** copolymer	1.5×10^5	7.4×10^4	2.0	865	21

$(J \propto (V)^{37})$. This fact makes the device particularly interesting for switching applications, as it resembles an ideal diode.

4.7.2 Doped PPV. The doping of PPVs can raise the electrical conductivity from 10^{-12} to as high as 10^3 S cm^{-1} depending on several factors such as the nature of the dopant, the nature and size of the group(s) attached to the polymer backbone, whether the polymer has been aligned (by stretching) or not and the effective conjugation length. Generally, the stronger the dopant oxidizing power, the higher the final conductivity. Thus, for instance, PPV (**35P**) pressed disks doped with I_2, BF_3 and SO_3, by exposure to their vapours, showed conductivities of 5×10^{-6}, 7×10^{-3} and 2×10^{-2} S cm^{-1}, respectively.[19] Electron-donating groups such as alkoxy increase the conductivities of PPVs doped with weak Lewis acids (*e.g.* I_2, BF_3), while electron-withdrawing substituents, as NO_2, do the opposite.[36] Plots of log(conductivities) *vs.* Hammett σ values have shown a distinct dependence between conductivity and polar substituent effect.[19] Studies with PPV model compounds[19,72] have shown that 7–9 conjugated double bonds are sufficient to ensure conductivity values similar to those of the corresponding polymers. For soluble PPVs blends with bulk polymers (*e.g.* poly(vinyl alcohol)) have been prepared and doped; the addition of as little as 10% (w/w) is sufficient to give a conductivity close to that of the PPV alone.[19]

4.8 GPC and elemental analysis

The molecular size of insoluble polymers is difficult to obtain. In such cases where elemental analyses showed small amounts of residual bromine due to unreduced end groups ($-CH_2Br$ for PPXs and $-CHBr_2$ for PPVs) and the C : H ratios were consistent with those calculated for the linear polymer structures, a rough estimation of the average molar mass and degree of polymerization was possible. Some examples are shown in Table 5.

Soluble polymers (or soluble fractions) could be analyzed by gel permeation chromatography (GPC) and some of these showed much higher average molar masses than the insoluble ones, suggesting that the polymerization process halts once the chain has grown sufficiently to reach insolubility. The results of average molar mass and polydispersity for some soluble PPXs and PPVs are summarized in Table 6.

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