Chemical modification of copoly(styrene-2,4,5-trichlorophenyl acrylate) to give polymers which are potentially electroactive

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The synthesis and derivatization of copoly(styrene-2,4,5-trichlorophenyl acrylate) (1) is described to obtain a new class of reactive and electroreactive polymers. Thus, the equimolar copolymerization of styrene and 2,4,5-trichlorophenyl acrylate in chlorobenzene, at 60°C in the presence of AIBN for 15 h, furnished the predominantly alternate copolymer in nearly quantitative yields. Complete displacement of the trichlorophenoxy (activating) groups by functional group carrying nuceophiles, for example 4-(2-aminoethyl)pyridine, histidine methyl ester, or 3-formamidopropanol, was carried out to produce the corresponding polymer derivatives with relatively high degrees of functionality. Alternatively, 1 was first partially reacted with a simple (structural) amine, such as morpholine or benzylamine, followed by reaction with a functional group carrying amine, or vice versa, to produce reactive polymers with relatively lower degrees of functionality, for example, anthraquinone, triethylenetriamine, or di-(2-hydroxyethyl)amine. Reaction of 1 with haloethylamines produced halogen carrying oligoimine grafts on the polymer backbone. The above named formamido polymer was further transformed to its isonitrile derivative. The hydroxy and halogen containing polymers were converted to the corresponding diphenylphosphine derivatives (the former via tosylation). The polymers carrying isocyano, amine, bidentate phosphine, or multidentate amine/phosphine ligands were reacted with Pd(II) or Cu(II), to obtain polymeric complexes containing *ca.* 3–20% complexed metal. The covalent attachment of polymers to amine-carrying electrodes, by active ester aminolysis, or by four component condensation is also briefly described.

(Keywords: copoly(styrene-2,4,5-trichlorophenyl acrylate); electroactive polymers; 2,4,5-trichlorophenyl acrylate copolymers; polymer-modified electrodes)

INTRODUCTION

Recently we have reported the synthesis of two series of electroreactive polymers[1,2] suitable for the preparation of modified electrodes[3]. These polymers, containing groups which can accept or donate electrons from or to an electrode, were derived from either (i) copoly(chloromethylstyrene–styrene)[1], or (ii) copolymers[2] of maleic anhydride with ethylene, ethyl vinyl ether or 1-vinyl-2-pyrrolidone. Since then we have prepared a new class of electroactive polymer by employing an approximately equimolar copolymer (1) of styrene and 2,4,5-trichlorophenyl acrylate. Soluble copolymers of the latter monomer, and those of other activated acrylates and methacrylates, have been previously suggested for the preparation of polymer-bound drugs[4–6]. More recently, several crosslinked and beaded analogues of 1 have been prepared[7,8], and have been found to be particularly suitable for the preparation of polymer-supported transition metal complexes[9], and for the synthesis of polymer supports/polymeric reagents of potential interest in peptide synthesis[10,11]. Copolymerization reactivity ratios of styrene and 2,4,5-trichlorophenyl acrylate have been studied in detail, and it has been found[12] that by using an equimolar mixture of the monomers, a predominantly alternating copolymer is formed. This copolymer (1) provides a relatively high degree of potential functionality, which may be utilized to obtain highly functionalised and potentially electroreactive polymers. Alternatively, the potentially reactive groups on the polymer may be diluted by structural units and less highly functionalized derivatives obtained. In this case, it is also possible to choose the structural units in such a way as to adjust the hydrophilic/hydrophobic balance of the polymer backbone. The synthesis of a number of such derivatives carrying anthraquinone functionality, or nitrogen and/or phosphine ligands, is reported in this paper, together with the preparation of several copper(II) and palladium(II) complexes of these polymeric ligands. The attachment of (potentially) electroreactive polymers to the electrode surface by active ester aminolysis, or four component condensation (4CC), is also briefly described.

EXPERIMENTAL

Materials

2,4,5-Trichlorophenyl acrylate[4] and 3-formamidopropanol were prepared as described previously. Dimethylformamide (DMF) and dichloromethane (DCM) were Analar grade, and used as received. Tetrahydrofuran (THF) (BDH, 99.7%) was refluxed over calcium hydride for 24 h, and distilled immediately prior to use. A solution of diphenylphosphine[1]/potassium tert-butoxide was prepared as follows: THF was flushed with argon for 20 min, diphenylphosphine (0.5 mmol ml^{-1}) and potassium tert-butoxide (0.5 mmol ml^{-1}) were added, and the mixture was stirred for 30 min under argon before it was used for phosphination reactions. The amines were laboratory reagents, and were used as received from the suppliers.

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Polymer characterization and analysis

These measurements were carried out as described previously[1].

Copoly(styrene-2,4,5-trichlorophenyl acrylate) (*1*). A solution of styrene (4 g, 38.5 mmol), 2,4,5-trichlorophenyl acrylate (10 g, 40 mmol), and AIBN (1.5 g, 9.1 mmol, ~0.13 M concentration) in chlorobenzene (56 ml), in a conical flask, was flushed with nitrogen for *ca.* 15 min. This was tightly stoppered, and kept at 60°C (water bath) for 15 h. The resulting polymer solution was then cooled to room temperature, and was precipitated into a large excess of methanol. This was allowed to stand at 0°C for 2 h, filtered and washed with methanol several times, and dried in a vacuum desiccator at room temperature to obtain an almost quantitative yield of the polymer.

Terpoly(styrene-acrylomorpholide-2-acrylamidoanthraquinone) (**2a**). The activated polymer **1** (3.2 g, ~ 10 mmol) and 2-aminoanthraquinone (~ 12 mmol) were dissolved in a minimum volume of dimethylformamide/triethylamine (4:1, v/v), and maintained in an oil bath at 56°C. The reaction was found (by i.r. spectroscopy of the precipitated polymer, see below) to proceed to *ca.* 50–60% after 3 h, and to *ca.* 90–95% after 28 h. The reaction mixture, after 28 h, was allowed to cool, and poured dropwise into excess 1 M sodium hydrogen carbonate, while stirring. The precipitate was allowed to settle, filtered, and dried. This was dissolved in DMF, followed by precipitation into excess 1 M hydrochloric acid, filtration, and drying. The intermediate product, which contained about 5–10% of the initial activated residues, was dissolved in DMF/morpholine (~ 5:1 v/v), and was allowed to stand at room temperature for 6 h. Most of the DMF and morpholine were removed under reduced pressure, the residue was stirred in *ca.* 50 ml of 1 M sodium hydrogen carbonate for about 30 min and extracted with DCM (20 ml × 3). The combined extract was washed with water (× 2), dried over magnesium sulphate, and filtered. The solvent was removed under reduced pressure, the residue was stirred in 10 ml ether for 10 min, filtered, washed with petroleum ether (b.p. 40°C–60°C) and dried; yield 2.19 g.

Copoly[styrene-4(2-acrylamidoethyl)pyridine] (**2b**). The activated polymer **1** (1 g) was dissolved in DMF/triethylamine (4:1, 6 ml), 4-(2-aminoethyl)pyridine (0.79, 0.2 eqs.) was added, well mixed and the reaction mixture was allowed to stand at room temperature for 24 h. It was then added dropwise into excess sodium hydrogen carbonate solution; the precipitate was filtered, and dried briefly. This was dissolved in chloroform, dried with magnesium sulphate, concentrated, and the polymer was precipitated into diethyl ether; yield 610 mg.

*Copoly(styrene-*N*-acryloylhistidine methyl ester hydrochloride)* (**2c**). Histidine methyl ester dihydrochloride (1.29, ~ 5 mmol) and potassium tert-butoxide (1.1 g, ~ 10 mmol) were stirred in DMF (20 ml) for 30 min. The salt was removed by filtration, and the solution was concentrated (at reduced pressure at 30°C) to about 10 ml. The activated polymer **1** (1 g) was added to the solution, and the reaction mixture was allowed to stand at room temperature for 48 h. The solvent was removed under reduced pressure (at ~ 50°C). The residue was dissolved in DMF/methanol (1:2, 3 ml), and the solution was added dropwise to excess 0.5 M sodium hydrogen carbonate. The precipitated polymer was filtered, briefly dried, and dissolved in DCM, dried over magnesium sulphate, filtered, and the solvent was removed under reduced pressure. This was dissolved in a methanolic solution of hydrochloric acid (~ 30 mmol in 30 ml, generated *in situ* from acetyl chloride), and allowed to stand for 2 h. The solution was then subjected to evaporation under reduced pressure. The residue was kept in dry diethyl ether for 24 h, at 0°C, filtered, washed with dry diethyl ether, and dried in a vacuum dessicator over phosphorus pentoxide; yield 800 mg. In two preparations, when the product was stored in the free base form, it became insoluble within two weeks. However, the solubility of the polymer hydrochloride was found to remain apparently unchanged during 8 months.

*Tetrapoly[styrene-benzylacrylamide-*N*′-(acryloyl-triethylenetetramine)-*N^1*,*N^4*-(bis-acryloyl-triethylenetetramine)]* (**2d**). The activated polymer **1** (0.5 g, 1.41 mmol g) was dissolved in DMF (2.5 ml) and the solution was allowed to stir for 2 h. A solution of benzylamine (107 mg, 1 mmol) and triethylamine (30 mg, 3 mmol) in DMF (2.5 ml), was then added to the vigorously stirred polymer solution, and the reaction mixture was left for 24 h at room temperature, or 4 h at 50°C. In either case, this reaction was found to proceed quantitatively (within experimental error). This solution was added, dropwise, into an ice-cooled, and vigorously stirred solution of triethylenetetramine (750 mg, ~ mmol) in DMF (5 ml), and the mixture was allowed to stir for 2 h. The solvent, and part of the triethylenetetramine, was removed under reduced pressure at 70°C, by evaporation and coevaporation with water, and with methanol. The residue was stirred with excess 1 M sodium hydrogen carbonate for 15 min. The precipitate was recovered by filtration, washed with water, briefly dried, and re-dissolved in DCM. The solution was dried over magnesium sulphate, concentrated, and precipitated into petroleum ether (b.p. 40°C–60°C), recovered by filtration, washed, and dried; yield 183 mg.

Copoly(styrene-2-chloroethylacrylamide) (**2e**). 2-Chloroethylamine hydrochloride (0.8 g, ~ 7 mmol) and potassium tert-butoxide (0.67 g, ~ 6 mmol) were mixed in DMF (10 ml), in an ice-bath, and the mixture was stirred for 15 min at room temperature. The solution of the resulting free amine was directly filtered into the activated polymer (1 g), and the mixture was allowed to stand at room temperature for 48 h with occasional mixing. The solvent was then almost totally removed under reduced pressure at 25°C, the residue was dissolved in acetone/methanol (2:1, 6 ml), and the polymer was precipitated into 0.5 M sodium hydrogen carbonate, followed by filtration. The crude precipitate was dried briefly, dissolved in dichloromethane (50 ml), dried over magnesium sulphate, filtered, and the solution was concentrated to *ca.* 6–7 ml. This was poured dropwise into diethyl ether (100 ml), the polymer was allowed to settle, filtered, and dried in a vacuum oven at room temperature; yield 384 mg.

Attempted preparation of copoly(styrene-2-bromoethylacrylamide) (**2f**). This preparation was carried out in a manner similar to that of **2e**, but the reaction proceeded less satisfactorily.

Terpoly[styrene-benzylacrylamide-di-(2-hydroxyethyl-) acrylamide)] (**2g**). Partial aminolysis of the activated polymer **1** (0.5 g) was carried out in the same way as for **2d**. The resulting solution was added dropwise into a vigorously stirred, and ice-cooled solution of diethanolamine (1 g, ~ 10 mmol) in DMF (75 ml), and the mixture was allowed to stand for 5 days at room temperature. Excess benzylamine was then allowed to displace the residual (*ca.* 5%; i.r.) activated groups on the polymer. DMF was removed under reduced pressure (at 50°C), and the residue was dissolved in methanol (2.5 ml), followed by precipitation into 0.5 M sodium hydrogen carbonate, filtration and drying; yield 21 mg.

Copoly(stryene-1-(dihydroxymethyl)ethylacrylamide) (**2h**). This was obtained in the same way as **2g**.

Terpoly(styrene-isocyanopropylacrylate-3-formamidopropyl acrylate) (**2i**). A mixture of the activated polymer **1** (3 g), 3-formamidopropanol (3 g, 30 mmol), triethylamine (3 ml, ~21 mmol), and DMF (3 ml) was heated at 105°C (oil bath) for 18 h. The reaction mixture was allowed to cool to room temperature, and the polymer precipitated into 1 M sodium hydrogen carbonate. The gummy material was dissolved in chloroform, dried over magnesium sulphate, filtered, and the solvent was removed to obtain the formamido derivation **2i**. The formamido polymer (**2i**, 0.6 g, ~2.3 mmol) was dissolved in pyridine (3 ml), and the solution was maintained in a water bath at ~10°C. Toluenesulphonyl chloride (0.7 g, 3.7 mmol) was added while stirring, and the reaction mixture was allowed to stir for 15 min at ~10°C. This was diluted with methanol (100 ml), followed by addition of 1.5% potassium chloride solution (40 ml). The precipitated polymer was recovered and dissolved in chloroform (20 ml). The solution was dried over magnesium sulphate, followed by filtration, and the solvent was removed. The residue was dissolved in acetone (2 ml), the polymer was precipitated into diethyl ether (80 ml), filtered, washed with diethyl ether, and dried in a vacuum desiccator at room temperature; yield 396 mg.

Phosphinated polymers **4e** *and* **4f**. The chloroethyl-polymer **2e**, (360 mg, ~1.5 mmol) was added to a THF solution of diphenylphosphine/potassium tert-butoxide (~3.9 mmol) under argon, and maintained at 75°C for 1 h. Additional THF (10 ml, de-aerated by argon) was added, and the mixture maintained at 65°C overnight (*ca.* 15 h). This was allowed to cool to room temperature, diluted with THF, filtered, the volume reduced to *ca.* 5 ml, and the polymer was precipitated into petroleum ether (40°C–60°C, 100 ml), filtered, and dried. The crude product was further purified by dissolution in THF (3 ml), precipitation in water (100 ml), dissolution in DCM, drying over magnesium sulphate, exchange of DCM with THF, and precipitation into petroleum ether; yield 210 mg. **4f** was prepared similarly, except that the reaction was allowed to proceed for 48 h at room temperature.

Terpoly[styrene-benzylacrylamide-bis-(2-diphenylphosphinoethyl)acrylamide] (**6**). The hydroxyethyl polymer **2g** (obtained from 2 g of **1**) was dissolved in pyridine/DCM (1:1, 10 ml), toluenesulphonyl chloride (0.89 g, 4.2 mmol) was added, the reaction mixture was stirred at room temperature for 2 h, and then kept at 0°C for 20 h. Pyridine was removed by co-evaporation with dioxane, under reduced pressure at 30°C. The residue was dissolved in acetone (5 ml), and the polymer was precipitated into 0.5 M sodium hydrogen carbonate. The tosylated polymer was purified by dissolution in DCM, drying over magnesium sulphate, filtration, and evaporation of the solvent under high vacuum. This was then converted to the phosphinated polymer **6**, by a procedure essentially similar to that described above for the conversion of **2e** to **4e**; yield 1.12 g.

Polymeric copper complex **7**. A solution of the imidazol-bearing polymer **2c** (200 mg, ~0.60 mmol) in DCM (15 ml) was added dropwise into a stirred solution of cupric acetylacetonate (26 mg, 0.1 mmol) in DCM (10 ml), and the reaction mixture was stirred at room temperature for 2 h. The solution was concentrated (~4 ml), and the polymer was precipitated into diethyl ether (100 ml), followed by washing with ether, and drying; yield 210 mg.

Polymeric copper complex **8**. A solution of the amino polymer **2d** (100 mg) in DMF/methanol (1:2, 3 ml) was added dropwise into a stirred solution of cupric sulphate pentahydrate (2.5 mg, 0.1 mmol) in water (3 ml), leading to immediate precipitation. The mixture was diluted with water (50 ml), stirred for 10 min, decanted twice, filtered, washed with water, and dried under vacuum at 30°C; yield 85 mg.

Polymeric palladium complex **9**. A solution of **3** (200 mg) in acetone (5 ml) was added to potassium tetrachloro-palladate (300 mg, 0.9 mmol) in water (5 ml) while vigorously stirring. The precipitated polymeric complex was washed with water and acetone, several times alternately, and dried in a vacuum desiccator at room temperature; yield 200 mg.

Polymeric palladium complex **10**. A solution of phosphinated polymer **4e** (102 mg) in DCM (3 ml) was added dropwise into a stirred solution of bis(benzonitrile) palladium (II) chloride (48 mg, 0.12 mmol) in DCM (2.5 ml), which led to immediate precipitation. The mixture was diluted with DCM (25 ml), stirred for 10 min, filtered, washed with a 1:1 mixture of ethyl acetate and petroleum ether, and dried; yield 80 mg.

Polymeric palladium complex **11**. A solution of the amine/phosphine containing polymer (**4f**/210 mg) in DMF (20 ml) was added dropwise to a stirred solution of bis(benzonitrile)palladium(II) chloride (96 mg, 0.25 mmol) in DCM (5 ml). The solvent was almost totally removed under vacuum at 30°C, the residue dissolved in DMF/DCM (1:1, 5 ml), and precipitated into a 1:1 mixture of ethyl acetate and petroleum ether (40°C) followed by filtration, washing with the same solvent, and drying; yield 180 mg.

Polymeric palladium complex **12**. This was prepared in the same way as **11**, except that 125 mg (0.27 mmol) polymer in 10 ml DCM and 50 mg (0.13 mmol) palladium complex in 10 ml DCM were used, and that the residue in 2 ml DCM was precipitated into 75 ml precipitant; yield 130 mg.

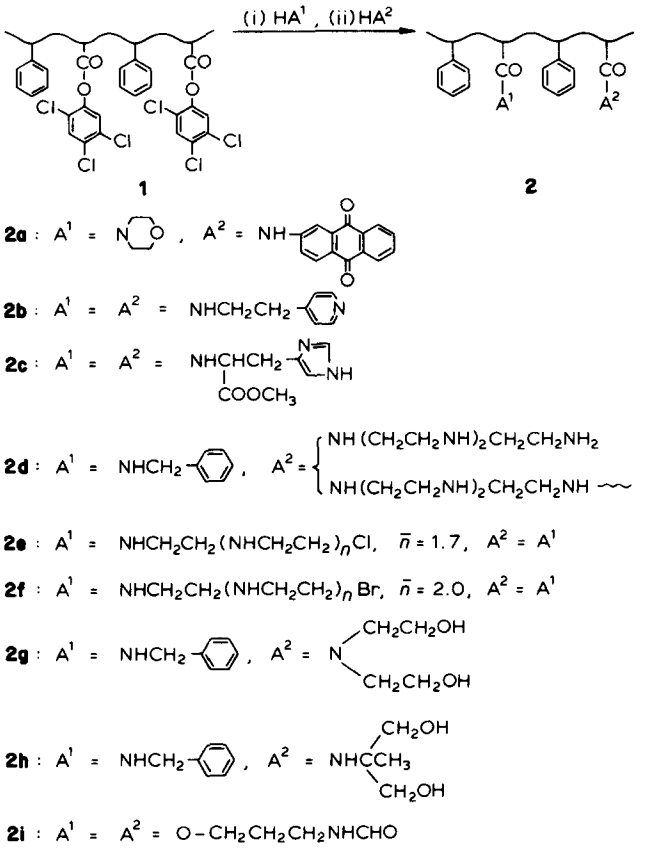
RESULTS AND DISCUSSION

Preparation and derivatization of copoly(styrene-2,4,5-trichlorophenyl(acrylate) (*1*)

The activated polymer **1** was obtained by copolymerization of the corresponding monomers in

chlorobenzene, at 60°C, and in the presence of AIBN. The polymerization conditions were chosen in such a way (see Experimental section) as to obtain relatively low molecular weight polymers ($\bar{M}_w = 20\,400$, $\bar{M}_n = 7970$), which are thought to have enhanced site accessibility on the electrode surface.

Aminolysis and *trans*-esterification of the activated polymer **1** was carried out according to *Scheme 1*, to obtain the polymer derivative **2**. Preparative details of the derivatives are given in the Experimental section and their composition and characteristic infra-red (i.r.) absorptions



Scheme 1 Derivatization of copoly(styrene–2,4,5-trichlorophenyl acrylate) (**1**)

are summarized in *Table 1*. Among these derivatives, **2a** is directly electroreactive due to the quinonoid groups, **2b–2d** carry amine ligands, **2g–2i** are precursors to phosphine ligands, **2e–2f** carry nitrogen ligands and are precursors to phosphine ligands, whilst **2i** can be transformed to isocyano (isonitrile) ligands.

From the wide range of derivatives shown in *Scheme 1*, it is apparent that the trichlorophenoxy activated polymer **1** provides a highly versatile polymer intermediate for the preparation of tailor-made electroreactive polymers, and reactive polymers in general. It should be emphasized, however, that the efficiency of nucleophilic displacement of the trichlorophenoxy groups is markedly dependent on the nature of the nucleophile, as can be inferred from the experimental conditions employed for the preparation of the various derivatives. For example, for many aliphatic amines the reactions proceed readily at, or below, room temperature, but it is impracticable in the presence of aromatic amines, under otherwise similar conditions. The latter aminolysis reactions, as well as certain *trans*-esterifications with alcohols, may be carried out satisfactorily in the presence of a catalyst, such as triethylamine, and at temperatures of 50°C–100°C. For many practical purposes, if the reaction does not proceed in the presence of less reactive nucleophiles, the reaction mixture may be reacted with a simple amine such as benzylamine, morpholine, etc. to displace the residual trichlorophenoxy groups on the polymer. It is also interesting to note that the reaction of less reactive nucleophiles with **1** is considerably more efficient if the polymer is first partially aminolysed with a simple amine. The reasons for this enhancement has been briefly discussed in ref. 8.

Some of the reactions shown in *Scheme 1* may be accompanied by side reactions. For example, reaction of **1** with multifunctional reagents, such as triethylene-tetramine, leads to polymer crosslinking. In concentrated polymer solutions, interchain crosslinking occurs, and insoluble polymers are formed, whilst in dilute polymer solutions, intrachain crosslinking (cyclization) takes place. Under these latter conditions the polymer remains soluble, but carries a lower number of free amino groups

Table 1 Polymer derivations prepared by nucleophilic substitution of the trichorophenoxy groups on the activated polymer **1** (see *Scheme 1*) and subsequent modification (see *Scheme 2*)

Polymer derivative	Composition (%)[a]					Functionality (mmol g^{-1})	Characteristic i.r. (cm^{-1})[c]
	C	H	N	Cl	P		
1			0.26	30.62		2.82	1760
2a						1.82	1590, 1630–60, 1720
2b						3.57	1520–60, 1605, 1660
2c	60.12	7.83	7.34	11.05		2.74	1665, 1730
2d	69.41	6.66	6.81			1.05	
2i	68.64	7.20	4.96			3.86	1670, 1730
3	69.67	6.95	4.57			3.00[d]	1670, 1730, 2140
4e	72.38	6.93	5.36	1.64	6.87		1435, 1450, 1490, 1650
4f	(66.48	6.51	9.35)[e]		4.72[f]		
5						0.82	1010, 1035, 1650
6	73.67	6.50	3.06		6.76[g]	0.80	1025, 1435, 1450, 1650

[a] Microanalytical data; most of nitrogen values are low due, probably, to problems related to complete decomposition of the polymers
[b] Theoretical values based on the functionality of the activated polymer **1**
[c] In nujol in the presence of small amounts of dichloromethane, or films obtained by evaporation of a dichloromethane solution of the polymer on the NaCl plates (for the phosphinated polymers)
[d] Approximate value estimated from the i.r. spectrum at 1730 cm^{-1}
[e] Based on the brominated polymer **2f**
[f] Based on the polymeric palladium complex **11**
[g] This is the equivalent of 1.1 mmol g^{-1} bidentate phosphine (see text for discussion)

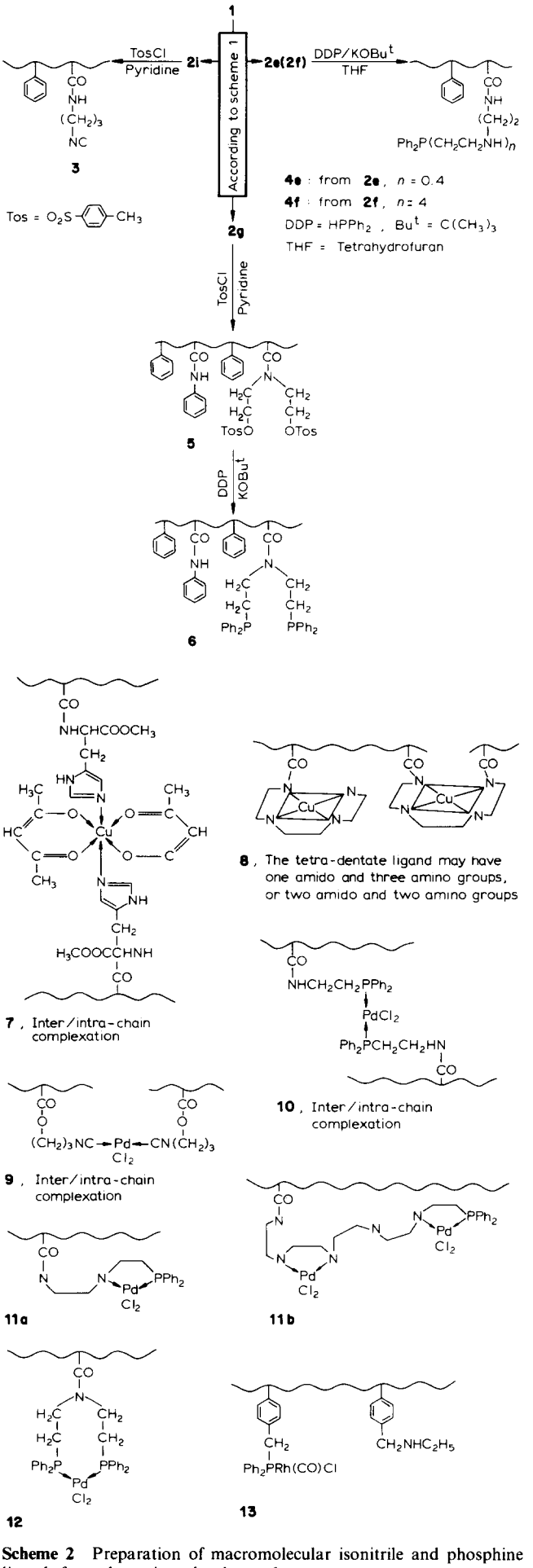
than expected. These intrachain crosslinking reactions are basically similar to those described in the case of the chloromethylated polymers[1], and profoundly affect the three-dimensional shape, and thus the apparent molecular weights[13], of the polymer. Crosslinking reactions are also likely to occur with aminoalcohols such as HA[2] in **2g** and **2h**. However, microanalytical data and particularly i.r. spectroscopy indicate that when the activated groups on the polymer are diluted from *ca.* 2.8 mmol/g to *ca.* 1 mmol/g, and under the indicated experimental conditions, crosslinking either does not occur, or is negligibly low.

Reaction of the activated polymer **1** with haloalkylamines is complicated by oligomerization of the haloalkylamines under the reaction conditions. This oligomerization, although it limits the use of this reaction for general synthetic purposes, provides an interesting route for the preparation of phosphine/amine multidentate ligands, as will be discussed in a later paragraph. As a side reaction, however, it can probably be adequately suppressed, in the case of chloroalkylamines, by optimization of the reaction conditions, selective catalysis, etc. By analogy with the multifunctional reagents referred to above, the polymer-bound oligoimines may also lead to polymer crosslinking. However, no insoluble polymers were formed during the preparation of **2e–2f**, and since these preparations involved the use of relatively highly concentrated polymer solutions, it may be concluded that no significant degree of intrachain crosslinking takes place either. This further suggests that aminolysis of the activated groups on **1** takes place considerably faster than the formation of the oligoimine grafts.

Preparation of macromolecular isonitrile and phosphine ligands

The preparation of the isocyano and phosphine derivatives of **1** is outlined in *Scheme 2*. Conversion of **1** to the isonitrile (isocyanide) derivative **3** was achieved via the intermediate **2i**; i.e. by reaction of **1** with 3-formamidopropanol followed by dehydration of the formamide with 4-toluenesulphonyl chloride. This dehydration procedure, adopted for the preparation of crosslinked isocyano polymers[14], is not completely satisfactory for soluble polymers. The recovery of the soluble isocyano polymer from the reaction mixture (excess tosyl chloride in pyridine) is considerably more difficult than that of a crosslinked polymer, and the use of other dehydrating reagents[15] may be more suitable for the preparation of soluble isocyano polymers. However, the isocyano derivative **3**, in which about 20% of the formamide groups remained unreacted, was presently prepared by using a smaller quantity of tosyl chloride, as described in the Experimental section.

For the preparation of tert-phosphine derivatives from the activated polymer **1**, several synthetic routes were investigated. A basically preferred route is the reaction of the polymer with suitably functionalized phosphine derivatives, such as 2-diphenylphosphinoethylamine or bis-(2-diphenylphosphinoethyl)amine[16]. However, this type of phosphine derivative is not readily accessible. Reaction of **1** with haloalkylamines, followed by phosphination, was found to be complicated, as referred to in the preceding section. Nevertheless, this route may be employed to obtain multidentate ligands, such as **4**, in



Scheme 2 Preparation of macromolecular isonitrile and phosphine ligands from the activated polymer **1**

which one ligand is a tert-phosphine and the others amine. In addition, this type of dually functionalized polymer is also suggested to provide an interesting alternative to the styrene based phosphine–amine resin 13 (ref. 17) employed for the so-called Aldox process.

The recently reported synthetic strategy[9], based on a tosyl intermediate, is more generally applicable, and this route was currently employed for the preparation of the bidentate phosphine derivative **6**, as shown in *Scheme 2*. The higher than expected phosphine content of **6** is thought to be related, at least in part, to the phosphination of the double bonds on the polymer chains. Due to the characteristic absorptions of the tosyl intermediate **5**, and the phosphinated product **6**, in the region 1000–1035 cm^{-1}, the tosylation and phosphination reactions can be readily monitored by infra-red spectroscopy, as noted in *Table 1* and more fully discussed in ref. 9.

Transition metal complexes of the macromolecular ligands

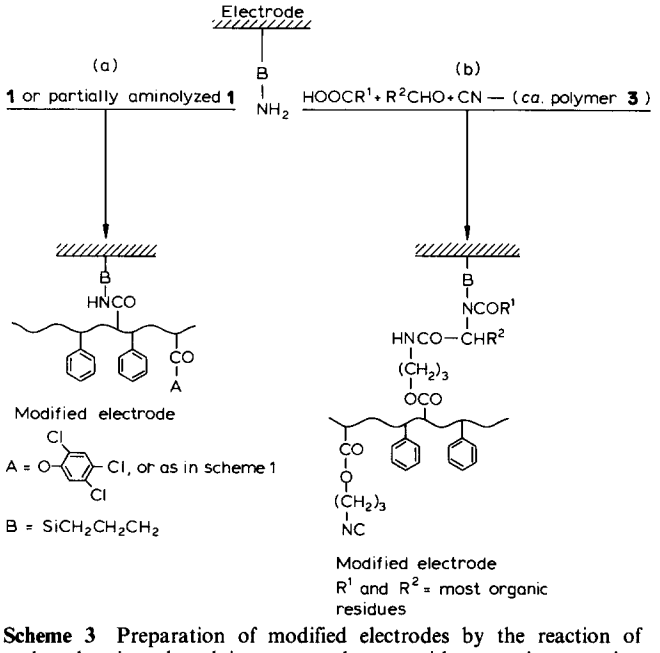
The details of a number of polymer-bound (polymeric) complexes obtained from the reaction of copper(II) and palladium(II) derivatives with the macromolecular ligands **2, 3, 4** and **6**, are summarized in *Table 2*, and their preparation is described in the Experimental section. The structures **7–12**, tentatively suggested for these complexes, are based on the ligand and metal content of the derivatives, as well as on the experimental procedures adopted for their preparation. In the case of the isonitrile complex **9**, i.r. spectroscopy showed a single isocyano absorption at 2246 cm^{-1} with an unresolved shoulder, indicating[18] that *ca.* 90% or more of the metal is coordinated by two, and *ca.* 10% by four, polymer bound isocyano ligands. The metal content for the polymeric complexes prepared from **4e** and **4f**, and the values calculated on the basis of structures **10, 11a, 11b** (see *Table 2*), are taken to indicate that the former preparation is composed of species **10** and **11a**, and that the latter preparation is composed of species **11a** and **11b**. Although analogous complex species may also be formed between two different polymer chains, these interchain complex species are expected to be relatively less stable, and thus rearrange to form the more stable bidentate (intrachain) analogues.

Table 2 Polymeric transition metal complexes obtained from the polymeric ligands **2c**, **2d**, **3**, **4** and **6** with palladium(II) and copper(II)

Polymeric complex	Polymeric ligand[a]	Metal substrate (MS)	Metal in the complex (%) Calc.	Found
7	**2c** (2.74)	$Cu(acac)_2$	2.81	3.21
8	**2d** (1.05)	$CuSO_4, 5H_2O$	5.52	5.23
9	**3** (3.00)	K_2PdCl_4	12.52	11.9
10	**4e** (2.22)	$PdCl_2(PhCN)_2$	9.72	12.2
11a / **11b**	**4f** (1.52)	$PdCl_2(PhCN)_2$	15.14 / 23.55	20.3
12	**6** (0.80)	$PdCl_2(PhCN)_2$	7.81[b]	10.3

[a] Theoretical ligand content of the polymer in mmol g^{-1} is given in parentheses

[b] From *Table 1* it is noted that analysis gives a value 1.1 mmol g^{-1} bidentate phosphine ligand for this polymer; the metal content of the polymer on that basis is 9.72%



Scheme 3 Preparation of modified electrodes by the reaction of carboxyl-activated and isocyano polymers with an amino carrying electrode

Preparation of modified electrodes

There are principally two ways[3] by which an electroreactive polymer may be introduced onto the electrode surface: (i) adsorption or absorption, and (ii) chemical (covalent) attachment. The former technique is simple and is usually satisfactory for most preliminary studies. According to this technique, the electrode is dipped in a suitable solution of the desired electroreactive polymer, followed by careful evaporation of the solvent. A polymer coat may also be formed on the electrode surface by electrochemical polymerization of a suitable monomer, using the electrode itself as an initiator. By this method it is possible to monitor, and thus to adjust, the thickness of the coat by adjustment of the electrochemical process. However, modified electrodes of potential interest are required to perform highly selective electrocatalytic processes (cf. ref. 19 and 20), and thus require carefully designed and tailor-made catalytic species on the polymer coat. Such tailor-made molecular constructions may not be feasible by electrochemical polymerization. More generally, however, covalent attachment provides a permanent coat, and is the method of choice for many systematic and long term studies. Covalent attachment requires the generation[3c] of a simple functionality, such as OH, COOH or NH_2, on the electrode surface, followed by reaction of the polymer with the functions. Some of the polymers described presently are suitable for covalent attachment to amine bearing electrodes by reactions not previously employed for this purpose. These are:

(i) Reaction of the electrode with polymer derivatives according to *Scheme 3a*. The polymer may be a partially functionalized derivative of **1**, or **1** itself, followed by (in the latter instance) the displacement of the trichlorophenoxy groups on the electrode surface.

(ii) Reaction of the electrode with the isocyano polymer **3**, by a four component condensation (4CC, cf. ref. 11), according to *Scheme 3b*.

Further details of these reactions and the characterization of the resulting modified electrodes will be reported elsewhere[21].

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