Synthesis of electroreactive polymers from poly (m,p-chloromethylstyrene) and copoly (m,p-chloromethylstyrene–styrene)

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Polymerization, and copolymerization with styrene, of m,p-chloromethylstyrene have been carried out at 75°C, in chlorobenzene and in the presence of AIBN ($[AIBN] \simeq 6 \times 10^{-2}$, and 12×10^{-2} M, respectively). The polymer molecular weights, determined by g.p.c., are: $\bar{M}_w = 8670$, $\bar{M}_n = 5860$, and $\bar{M}_w/\bar{M}_n = 1.48$ for the homopolymer, poly(m,p-chloromethylstyrene), (1a); and $\bar{M}_w = 8805$, $\bar{M}_n = 5144$, and $\bar{M}_w/\bar{M}_n = 1.71$ for the copolymer, copoly(m,p-chloromethylstyrene–styrene), (2a). A series of phosphine derivatives of both 1a and 2a are prepared by the reaction of the polymers with either chlorodiphenylphosphine/ lithium, or diphenylphosphine/potassium tert. butoxide. A number of other potentially electroreactive derivatives of 2a are obtained by reacting the polymer with 2-aminoanthraquinone, 3-N-methylamino-propionitrile, or 2-(2-aminoethyl) pyridine. The phosphinated polymers are reacted with bis-benzo-nitrilepalladium-(II) chloride to obtain a series of polymer–palladium(II) complexes containing 8.5–12.9% palladium. Similarly, reaction of the last-named bidentate polymeric ligand with cupric acetylacetonate, or cupric sulphate pentahydrate, produces polymer–copper(II) complexes having 5.8, or 3.3% copper, respectively. The inter/intra-chain nature of some of the side reactions during the derivatization of the chloromethylated polymers, and that of the complex formation between transition metal centres and macromolecular ligands, are briefly discussed in view of the experimental results.

(Keywords: synthesis; electroreactive polymers; poly(m,p-chloromethylstyrene–styrene); copoly(m,p-chloromethylstyrene–styrene))

INTRODUCTION

There has recently been increasing interest in the development of modified electrodes[1-3]. A modified electrode differs from a conventional electrode in that the electrode surface is altered in such a way as to provide a thin film between the metal surface and the bulk electrolyte. As a result the process of electron transfer between the Fermi level of the metal and the ions in the electrolyte is mediated by the suitably chosen film on the electrode surface. This principle provides a versatile means of modulating the kinetic behaviour of the electrode, and thus achieving higher efficiency, selectivity, and possibly catalysis in a given electrochemical process. Modification[1-3] of the electrode surface may be achieved by either covalent attachment or adsorption, of an electroreactive material to the electrode surface. In either case, the use of polymeric materials offers a number of advantages as compared with that of the low-molecular-weight compounds. The increased molecular size and binding ability of macromolecules permits the preparation of surfaces with increased stability and functional manoeuvrability. For example, the electrochemical process may be more easily modulated by adjusting the solvent/substrate compatibility[4] of the polymer, and/or having two (or more) types of electroreactive groups on the same polymer chains. Fabrication of substrate selective (enzyme-like) polymers[5] on the electrode surface may enhance selectivity of electro-organic synthesis and electro-analytical processes.

A large number of electroreactive polymers have so far been used for the preparation of modified electrodes. Currently, the development of versatile macromolecular precursors which can be readily derivatized to give a series of electroreactive polymers, appears particularly relevant. Among several reactive polymeric systems recently developed[6], for applications including the so-called solid phase technique[7], are polymers and copolymers based on (1) chloromethylstyrene[8], (2) maleic anhydride[9], and (3) 2,4,5-trichlorophenyl acrylate[4,10]. These polymers can easily be adopted for the preparation of polymeric materials suitable for electrode modification. The derivatization of these polymer systems has been studied and, therefore, a wide range of macromolecules carrying pendent electroreactive groups have been obtained. The present paper gives full details of the synthesis of poly(m,p-chloromethylstyrene) (1a) and copoly(m,p-chloromethylstyrene–50% styrene) (2a), and of the conversion of 1a and 2a to potentially electroreactive polymers carrying anthraquinone, tertiary phosphine, or bidentate nitrogen ligands. The preparation of a number of palladium (II) and copper (II) complexes of these polymeric ligands is also described. Details of the maleic anhydride copolymer system have recently been reported[11], while information concerning 2,4,5-trichlorophenyl acrylate copolymers and their derivations[12], together with electrochemical characterization[13], will be published shortly.

Type 1a and 2a polymers are analogous to the chloromethylated resins widely used as polymer supports[7], and can be obtained by either (co)polymerization of the

corresponding monomer(s), or chloromethylation of the more readily available polystyrene. Both routes are, however, complicated in practice. The synthesis of pure isomers of chloromethylstyrene is laborious[8], whereas chloromethylation of polystyrene involves the use of the carcinogenic reagent chloromethylether. Furthermore, chloromethylation of pre-formed polystyrene is accompanied by the formation of crosslinking (methylene bridges)[14] in the polymer. The use of a commercially available monomer mixture consisting of *meta* (60%) and *para* (40%) isomers has also been studied[8,15,16]. Direct chromatographic separation of this mixture is not practical due to the polymerization of the monomer in the column, but separation of the pure isomers via bromination/debromination of the mixture has recently been reported[16]. In the present study, the *meta/para* was, however, found to be satisfactory, and was used without separation of the isomers.

RESULTS AND DISCUSSION

Polymer synthesis and polymer molecular weights

Polymerization of *m,p*-chloromethylstyrene, and its equi-molar copolymerization with styrene, were carried out in chlorobenzene at 75°C, and in the presence of relatively high concentrations of bis-azo-isobutyronitrile ($[AIBN] \simeq 6 \times 10^{-2}$ M, and 12×10^{-2} M, respectively). Weight-average $(\bar{M}_w)$ and number-average $(\bar{M}_n)$ molecular weights of the resulting poly(*m,p*-chloromethylstyrene) (**1a**), and copoly(*m,p*-chloromethylstyrene-styrene) (**2a**) were determined by gel permeation chromatography (g.p.c.), and were as follows:

1: $\bar{M}_w = 8670$, $\bar{M}_n = 5860$, $\bar{M}_w/\bar{M}_n = 1.48$

2: $\bar{M}_w = 8805$, $\bar{M}_n = 5144$, $\bar{M}_w/\bar{M}_n = 1.71$

The relatively low-molecular-weight polymers thus produced were thought to have enhanced site accessibility on the electrode surface.
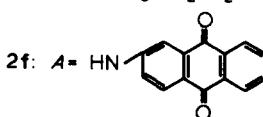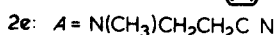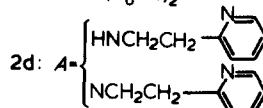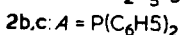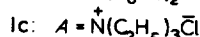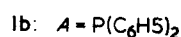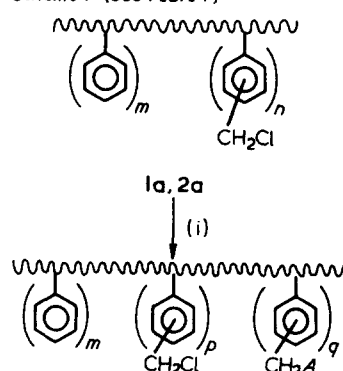
In principle, derivatization of the pendent chloromethyl groups on **1a** and **2a** should not affect the average length of the backbone polymer chains. Under the present experimental conditions some degradation/grafting may occur, but this is expected to have negligible or relatively small effect on backbone molecular weights. Preparation of the macromolecular derivatives to be discussed in this paper was usually accompanied by fractionation during the purification (precipitation) of the intermediates and the product. As a result the derivatized polymers are expected to have higher average molecular weights than the original polymers even allowing for the molecular weight increase due to the production of substituent pendent groups. Another event which may increase polymer molecular weights is when the chloromethyl groups from one polymer chain take part in side reactions involving other polymer chains. This happens, for example, during the preparation of the bidentate ligand **2d**. Furthermore, the formation of polymer–metal complexes may involve inter-chain co-ordinations (*cf.* **34** and **42**), which evidently have marked effects on the molecular weights of the polymers. These general remarks are substantiated by observations during the recovery of the derivatized samples, and by microanalytical data (*cf.* **31a** and **32a** in *Table 2*). Detailed analysis of the molecular weights and molecular weight distribution of the po-

lymers and their derivatives are being studied currently and will be reported in a subsequent paper.

Derivatization of the polymer-bound chloromethyl groups

Preparation of a series of potentially electroreactive derivatives of **1a** and **2a** is shown in *Scheme 1*. Fundamental composition and the characteristic infra-red (i.r.)

Scheme 1 (see Table 1)

1b: $A = P(C_6H5)_2$

1c: $A = \overset{+}{N}(C_2H_5)_3\bar{C}l$

2b,c: $A = P(C_6H5)_2$

2d: $A = \begin{cases} HNCH_2CH_2 \\ NCH_2CH_2 \end{cases}$

2e: $A = N(CH_3)CH_2CH_2C\,N$

2f: $A = HN$

(i) = HA, except for **1c** where it is $N(C_2H_5)_3$

absorption of the polymers are summarized in *Table 1*; and full details of their preparation is given in the Experimental section. Nucleophilic substitution of the chlorine atoms on chloromethylated polystyrene is used widely[7,*] to introduce various functional groups into crosslinked styrene-based resins. In principle, these reactions are expected to proceed relatively more smoothly on the presently described soluble polymers, than on crosslinked resins. In practice, preparation of derivatives of soluble polymers is considerably more difficult due to precipitation/recovery of the polymer, as well as the solubilizing effects of certain macromolecular derivatives. For example, parts of the lithium (or sodium) chloride formed during the preparation of **1b** and **2b–2c** are solubilized by the polymer in organic solvents, and are difficult to remove from the reaction mixture. Thus, the polymers had to be precipitated into water, followed by removal of the residual water from the polymer, using a drying agent (e.g. magnesium sulphate) in an organic solvent.

A more fundamental aspect of the reactions shown in *Scheme 1* is the possibility of side reactions which may not be equally likely on soluble and crosslinked polymers. Reaction of **1a** with the bidentate ligand 2-(2-aminoethyl)-pyridine, as shown in *Scheme 2*, represents an interesting example. At 45°C, and under the conditions similar to

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Table 1 Basic features of poly(m,p-chloromethylstyrene) (**1a**), copoly(m,p-chloromethylstyrene—styrene) (**2a**), and a number of their potentially electroactive derivatives **1b—1c**, and **2b—2f** (scheme 1)

Polymer	Mol fraction compositions[a] ($m+n=m+p+q=1$)		Degree of functionality[b] (mmol g^{-1})[a]			Characteristic i.r.[c] (cm^{-1})
	m	q	Cl	N[d]	P	
1a	0.00	0.00	6.42	—	—	1265
1b	0.00	0.85	0.48	—	2.72	1480, 1430
1c	0.00	1.00	4.02	4.06	—	1600—1750 (broad)
2a	0.50	0.00	4.15	—	—	1265
2b	0.50	0.26	1.56	—	1.59	1265, 1480, 1430
2c	0.50	0.50	0.00	—	2.43	1480, 1430
2d	0.50	0.50	0.00	1.95[e]	—	1585
2e	0.50	0.50	0.00	3.27	—	2145
2f	0.50					1665, 1585, 1260

[a] Based on elemental analysis, and in good agreement with the theoretical values where relevant

[b] Cl, N, and P represent the corresponding functional groups in the derivatives

[c] In nujol in the presence of small amounts of dichloromethane, or film obtained by evaporation of a dichloromethane solution of the polymer on the NaCl plates

[d] Excluding the nitrile (—CN) end groups which are about 0.4 mmol g^{-1} in the initial polymers **1a** and **2a**

[e] Calculated to represent 0.44 mmol g^{-1} single-bound (NH), and 1.51 mmol g^{-1} doubly-bound (N) nitrogen

those usually employed for crosslinked resins ($\approx$5-fold excess reagent, and 5 ml solvent per g polymer), the reaction led to the formation of a totally insoluble polymer, which was not studied further. In relatively dilute solutions (100 ml solvent per g polymer, see Experimental), the polymer remained soluble after complete substitution of the chlorine atoms, although the nitrogen content of the product indicates that $\approx$77% of the amino groups are doubly attached to the polymer. The structures involved in *Scheme 2* in dilute and

Scheme 2
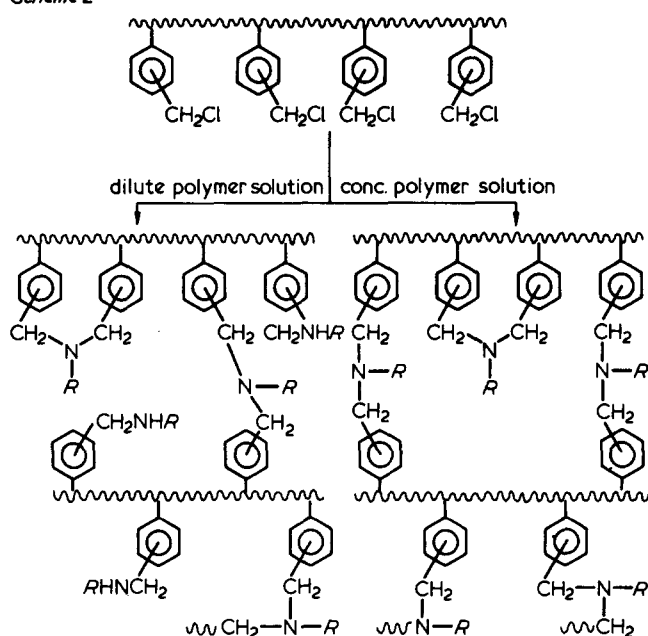
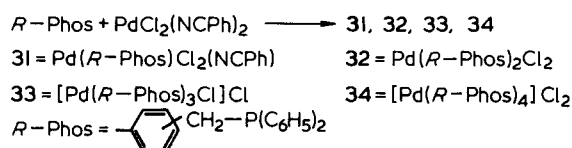
concentrated solution are represented by (I) and (II), respectively. Structure (II) contains relatively more intermolecular cross-links than structure (I). It is also noteworthy that when the reaction was stopped after partial substitution of the chlorine atoms, the purified polymer became cross-linked (insoluble) in the solid state, and at room temperature. (This facile crosslinking reaction may be useful for the preparation of crosslinked coats on an electrode surface.) A basically similar side reaction led to the formation of insoluble polymer during the preparation of the quarternary ammonium derivative **1c**,

apparently due to the presence of small amounts of secondary amines in triethylamine. This problem was, however, overcome by using a sample of carefully distilled triethylamine.

Preparation of transition metal complexes of the macromolecular ligands[17]

Important features of a series of palladium (II), and copper (II) derivatives of the polymeric ligands **1b**, **2b**, **2c** and **2d** are summarized in *Table 2*. In general, co-ordination of transition metal centres by macromolecular ligands may, depending on the reaction conditions, produce a mixture of several complex species*. This is indicated in *Scheme 3* for the co-ordination of the phosphinate polymers (**1b**, **2b** and **2c**) with palladium (II). An additionally interesting feature of these macromolecular complexes is the distribution of the intra-and inter-chain co-ordinations around each metal centre. This is not shown in *Scheme 3* for the sake of clarity, but the representation would basically resemble the type of structures illustrated in *Scheme 2*. However, the co-

Scheme 3

R—Phos + PdCl$_2$(NCPh)$_2$ ⟶ **31**, **32**, **33**, **34**

31 = Pd(R—Phos) Cl$_2$(NCPh)   **32** = Pd(R—Phos)$_2$Cl$_2$

33 = [Pd(R—Phos)$_3$Cl]Cl   **34** = [Pd(R—Phos)$_4$] Cl$_2$

R—Phos = CH$_2$—P(C$_6$H$_5$)$_2$

ordinated species shown in *Scheme 3* are not all equally stable, and in many cases relatively homogeneous polymer complexes can be obtained under carefully controlled experimental conditions. It is, for example, remarkable that the reaction of **2b** with excess bis-benzonitrilepalladium (II) chloride* produces, after fractionation, two polymeric complexes with metal:ligand ratios of 1:1, and 1:2, respectively.

A more complicating aspect of complex formation within the chains of macromolecular ligands is the possibility of some of the co-ordinating sites becoming

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* A noteworthy demonstration of this phenomenon is provided by transition metal complexes of macromolecular isocyanides, where the vibrational frequency of the isocyano ligand varies, in most cases, according to the type and number of ligands present in the complex (see ref. 18)

| Polymeric ligand[a,b]	Metal substrate	Polymeric complex	Metal in the complex (%) Calc.	Found
2b (1.59)	PdCl₂(CNPh)₂	**31a**	11.71	12.9
2b (1.59)	PdCl₂(CNPh)₂	**32a**	7.42	8.5
2c (2.43)	PdCl₂(CNPh)₂	**31b**	10.64	11.9
2d (1.95)	Cu(acac)₂[c]	**41**	6.74	5.8[d]
2d (1.59)	CuSO₄5H₂O	**42**	5.24	3.3[d]

[a] The ligand content of the polymer in mmol g⁻¹ is given in parentheses
[b] The polymers contain, in addition to the indicated ligands, ≈0.1–0.2 mmol g⁻¹ CN end groups which may take part in the co-ordination reactions
[c] acac = acetylacetonate
[d] The lower metal content is probably due to the inaccessibility of some of the polymer-bound ligands

isolated and inaccessible for co-ordination. This problem appears to be particularly pronounced in the case of the polymer–cupric (II) complexes **41** and **42** shown in *Scheme 4*. Here the lower than expected metal content of these complexes (see *Table 2*) is probably explained by the inaccessibility of some of the polymer-bound ligands, particularly in the case of **42**, where complexation of the polymer evidently leads to one crosslinked structure.
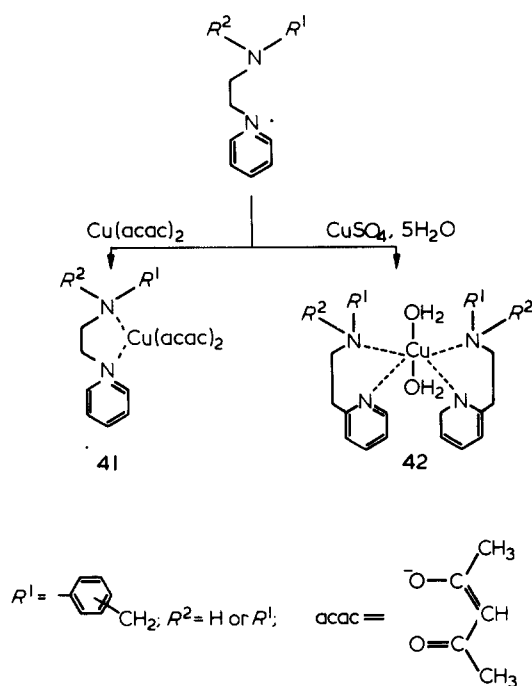
EXPERIMENTAL

Materials

Styrene (BDH or Aldrich) was washed with 5% (wt/vol) sodium hydroxide, and distilled under reduced pressure before use. Chloromethylstyrene (vinylbenzyl chloride, VBC, *meta:para* = 60:40) was obtained from Fluka, and was distilled under reduced pressure. Azo-bis-isobutyronitrile (AIBN) was recrystallized from ethanol. Triethylamine (Rose Chemicals) was distilled, and a mid-fraction was used. Diphenylphosphine was prepared as described in the literature[19], except that 30 g lithium per mol of triphenylphosphine was used, and the reaction was

allowed to continue for 20 h. The crude (undistilled) product was consistently found satisfactory for the phosphination reactions. Tetrahydrofuran (BDH, 99.7%) was refluxed over calcium hydride for 24 h, distilled, and used freshly. All other reagents and solvents were used as received.

Polymer characterization and analysis

Polymer molecular weights were determined by gel permeation chromatography, at the Polymer Supply and Characterization Centre, Shawbury, Shrewsbury, England. Metal analyses were carried out by Butterworth Laboratories, Middlesex, England. Infra-red (i.r.) spectra of the polymers were recorded on a Perkin Elmer 298 spectrophotometer, using a Nujol mull, or films formed from dichloromethane solutions of the polymer deposited on sodium chloride plates. All the analyses were carried out on polymer samples which had been dried to constant weight *in vacuo* at room temperature, except where stated otherwise.

Poly(m,p-chloromethylstyrene) (1a)

A solution of the monomer in chlorobenzene (1:2, vol/vol) containing 1% (weight per total volume) AIBN was flushed with nitrogen for 10 min, tightly stoppered, and polymerized at 75°C for 20 h. The solution was cooled to room temperature, diluted with two volumes of chlorobenzene, and the polymer was precipitated by dropwise addition into excess methanol. This was allowed to stand overnight, filtered, and the precipitate was washed with methanol four times, and dried in a vacuum oven at 40°C. Yields of >90% were generally obtained.

Copoly(m,p-chloromethylstyrene–50% styrene) (2a)

This polymer was prepared in a manner similar to that described for **1a**, except that 2% (wt/vol) initiator was used.

Phosphination reactions

Method A. A solution of the chloromethylated polymer **2a** (3.84 g, ≈15 m mol) in dry tetrahydrofuran (50 ml) was flushed with nitrogen for 10 min. Chlorodiphenylphosphine (3.31 g, 15 mmol), and lithium (130 mg, 18 mmol) were added to the polymer solution, and the mixture was stirred under nitrogen for 4 h. The flask was then tightly stoppered, and allowed to stir overnight, by which time all of the lithium had disappeared. The mixture was filtered, the solution was diluted to ≈70 ml by tetrahydrofuran, and added dropwise to water (1 l), while stirring. The coagulated polymer was removed from water, dissolved in ethylacetate (200 ml), and dried over magnesium sulphate. This was then filtered, the solution concentrated to ≈15 ml, and the polymer was precipitated into excess petroleum ether (40°–60°C), maintained at 0°C for 1 h. The polymer was filtered off, washed with the same solvent, and dried to give 4.2 g of the phosphinated polymer **2b**.

Method B. A mixture of diphenylphosphine (2.80 g, 15 mmol) and potassium tert. butoxide (1.34 g, 12 mmol) in tetrahydrofuran (25 ml) was stirred under argon for 30 min. The chloromethylated polymer **1a** (1.52 g, 10 mmol) was added and the mixture stirred at 50°C for 5 h. The mixture was cooled, filtered, and the solution was concentrated to ≈10 ml, and added dropwise to excess

water while stirring. The polymer was filtered, briefly dried, dissolved in tetrahydrofuran, and purified as described in method A, to obtain **1b** (2.2 g).

Reaction of triethylamine with **1a**

To a stirred solution of **1a** (1 g) and triethylamine (2 g) in dioxan (10 ml), isopropanol was added until the solution became slightly turbid (≈ 15 ml), and the mixture was maintained at 85°C for 15 h. The solution was concentrated, and the polymer was precipitated into excess diethyl ether, washed with ether (3 times), and dried to give a near quantitative yield of the quarternary ammonium polymer **1c**.

Reaction of 2-(2-aminoethyl)pyridine with **2a**

The chloromethylated polymer **2a** (512 mg, 2 mmol) was dissolved in dioxan (20 ml), and was allowed to stand for 1 h. A solution of 2-(2-aminoethyl)pyridine (1.22 g, 10 mmol) in isopropanol (30 ml) was added to the polymer solution in one portion and under vigorous stirring, and the mixture was then maintained at 50°C for 15 h. The solution was concentrated to ≈ 6–7 ml on the rotary evaporator and the polymer was precipitated into 5% (wt/vol) potassium hydrogen carbonate, followed by filtration, and drying. The product was again dissolved in tetrahydrofuran (4 ml), and precipitated into water–methanol (1:1, vol/vol), filtered, and dried to obtain 430 mg of **2d**.

Reaction of 3-N-methylaminopropionitrile with **2a**

3-*N*-Methylaminopropionitrile (830 mg, 10 mmol) in isoproponal (15 ml) was added to a solution of **2a** (512 mg, 2 mmol) in dioxan (10 ml), and the mixture was maintained at 50°C for 15 h. The solvent was almost totally removed on the rotary evaporator, the residue was dissolved in tetrahydrofuran (10 ml), potassium tert. butoxide (450 mg, 4 mmol) was added, and the mixture was allowed to stir at room temperature for ≈ 30 min.

Precipitation into 1.5% potassium chloride (wt/vol), filtration, washing with water (3 times), and drying, produced **2e**(450 mg).

Reaction of 2-aminoanthraquinone with **2a**

A mixture of **2a** (512 mg, 2 mmol), and 2-aminoanthraquinone (670 mg, 3 mmol) was dissolved in a minimum volume of dimethylformamide, and the solution was maintained at 50°C for 24 h. The reaction mixture was cooled, poured into excess methanol while stirring; the precipitate was filtered, washed with methanol, and dried. This was redissolved in dimethylformamide, followed by precipitation in methanol, washing, and drying to obtain **2f**, HCl (310 mg). The free amine form of **2f** was obtained by dissolving the hydrochloride in acetone, followed by precipitation in 1 M potassium hydrogen carbonate, filtration, and dried.

Polymer–palladium complexes **31a** and **32a**

A solution **2b** (360 mg, 0.57 mmol) in dichloromethane (10 ml) was added dropwise to bis-benzonitrilepalladium (II) chloride (192 mg, 0.5 mmol) in the same solvent (20 ml), while stirring, and the mixture was allowed to stir for 10 min. The solvent was removed under reduced pressure, the residue was dissolved in dimethylformamide (5 ml) and the solution was added dropwise to ethyl-

acetate (80 ml). This was maintained at 0°C for 4 h, filtered, and the precipitate washed with ether (3 times), and dried to obtain the polymer–palladium complex **32a** (200 mg). The filtrate was concentrated to about 5 ml, and added dropwise to diethylether (80 ml), allowed to stand for 4 h at 0°C, filtered, washed with ether (3 times), and dried to give **31a** (125 mg).

Polymer–palladium complex **32b**

The phosphinated polymer **2c** (200 mg, 0.49 mmol) in dimethylformamide (20 ml) was added dropwise to bis-benzonitrilepalladium (II) chloride (96 mg, 0.25 mmol) in dichloromethane (5 ml) while stirring, and the mixture was stirred for 30 min. The solvent was removed under vacuum, the residue dissolved in dichloromethane (5 ml), and the solution was added dropwise to petroleum ether (40–60°C)–ethyl acetate (1:1, 400 ml). This was maintained at 0°C for 1 h, filtered, washed with petroleum ether (2 times), and dried to obtain **32b** (300 mg).

Polymer–copper complex **41**

A solution of **2d** (106 mg, 0.207 mmol) in dichloromethane (10 ml) was added dropwise to cupric acetylacetonate (80 mg, 0.305 mmol) in dichloromethane (10 ml) while stirring, and the mixture was allowed to stir for 30 min. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (3 ml), and the polymer was then precipitated into excess diethyl ether (50 ml), kept at 0°C for 30 min, filtered, and dried to give **41** (80 mg).

Polymer–copper complex **42**

Cupric sulphate pentahydrate (50 mg, 0.2 mmol) in water (2 ml) was added dropwise into a solution of **2d** (150 mg, 0.30 mmol) in dimethylformamide (6 ml), and the mixture was stirred for 10 min. The solvent was removed under vacuum; the residue was stirred in water (5 ml) for 10 min, filtered, washed with water (3 times), and dried to produce **42** (138 mg).

ACKNOWLEDGEMENTS

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