Phthalocyanine-containing polystyrenes

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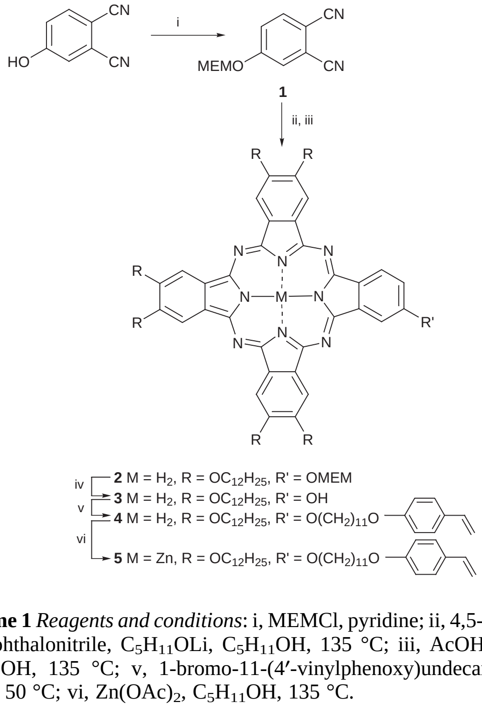
An unsymmetrical phthalocyanine derivative containing a single styrene unit, prepared using a mixed phthalonitrile cyclotetramerisation, can undergo free radical polymerisation to give well-defined polystyrenes in which the macrocyclic components aggregate even in dilute solution.

Phthalocyanine (Pc) and its derivatives possess interesting electronic, optical and catalytic behaviour.[1] There has been much interest in the synthesis of phthalocyanine-containing polymers suitable for the exploitation of Pc functionality.[2] Previously, Pc has been incorporated into intractable network polymers,[3] rigid polysiloxanes in which the silicon(IV) ion is held within the central cavity of the macrocycle,[4] main-chain liquid crystalline polymers,[5] polymers formed by the coordination of bidentate ligands with metal ion containing Pcs,[6] dendrimers which comprise a Pc ring at their core,[7] and polymers in which the Pc is a component of a side-chain attached to the polymer backbone.[8] Here we describe the synthesis of polystyrenes with Pc-containing side-chains. The widespread use of polystyrene as the substrate for polymer-supported catalysts, its excellent processability and its optical clarity make these materials attractive synthetic targets with numerous potential applications.

The synthetic route to the Pc-containing styrene monomers is given in Scheme 1. The strategy is to prepare an unsymmetrical phthalocyanine, which possesses six solubilising alkyl side-chains and a single reactive hydroxy functionality for the attachment of the styrene group, *via* a mixed cyclotetramerisation of suitable phthalonitrile precursors. In order to protect the hydroxy group during the base catalysed Pc forming reaction, 4-hydroxyphthalonitrile[9] was first reacted with methoxyethoxymethyl chloride (MEM chloride) to give **1**. The MEM moiety not only acts as a protecting group during the mixed cyclotetramerisation reaction between **1** and an excess of 4,5-bis(dodecyloxy)phthalonitrile[8] but its relative polarity, as compared to that of the dodecyloxy side-chains, also facilitates chromatographic separation of the required unsymmetrical Pc **2** from the Pc by-products.[10] Removal of the MEM group followed by the reaction of the resulting Pc **3** with 1-bromo-11-(4-vinylphenoxy)undecane[11] gives the desired Pc-containing styrene monomer **4**. Spectroscopic and elemental analysis of **4** was consistent with its proposed structure.†



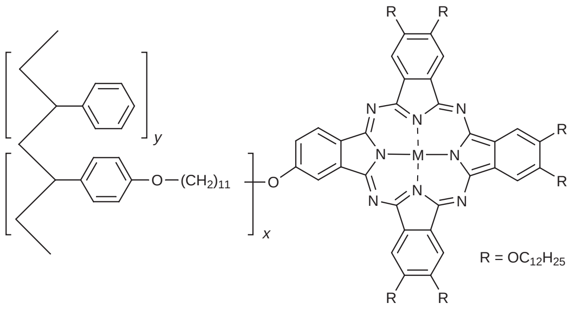
Scheme 1 *Reagents and conditions*: i, MEMCl, pyridine; ii, 4,5-bis(dodecyloxy)phthalonitrile, $C_5H_{11}OLi$, $C_5H_{11}OH$, 135 °C; iii, AcOH; iv, PPTS, $C_5H_{11}OH$, 135 °C; v, 1-bromo-11-(4′-vinylphenoxy)undecane, K_2CO_3, DMF, 50 °C; vi, $Zn(OAc)_2$, $C_5H_{11}OH$, 135 °C.

The long alkyl spacing group between the styrene unit and the Pc ring is designed to minimise any detrimental steric effect on the polymerisation reaction due to the large macrocycle. Indeed, free radical polymerisation of **4** can be achieved with high conversion (>85%) to give soluble polymers of reasonable molar mass ($M_n > 40 \times 10^3$ amu) and with relatively narrow polydispersity ($M_w/M_n \sim 1.5$) as measured by gel permeation chromatography (GPC) against commercial polystyrene standards (Table 1). The optimum conditions for polymerisation proved to be a 0.05 mmol ml^{-1} concentration of monomer **4** in benzene solution using a 5 mol% concentration of AIBN relative to **4**. Prior complexation of **4** to zinc(II), to give monomer **5**,† resulted in polymers of higher mass.

It is possible to vary the concentration of Pc functionality within the resulting materials by preparing random copolymers from styrene and Pc **4** or **5**. Interestingly, the molecular masses obtained for these copolymers were consistently higher than those of unsubstituted polystyrene obtained under the same conditions. This prompted us to perform control experiments in which styrene was polymerised with or without added unreactive metal-free octakis(dodecyloxy)-Pc (ODPc) or its zinc(II) derivative (ZnODPc). The polystyrene prepared in the presence of ODPc or ZnODPc proved to have significantly higher mass and lower polydispersity than that prepared in its absence (Table 1). This unexpected result was attributed to the Pc removing the residual oxygen which remained after conventional deoxygenation using a repeated freeze–thaw degassing process. It is well-established from various spectroscopic and electronic conductivity studies that Pcs interact strongly with molecular oxygen. Zinc(II)-containing Pcs are particularly efficient at interacting with oxygen and this may explain why monomer **5** is particularly well-suited to free radical polymerisation.

UV–VIS absorption spectra of the polymers dissolved in toluene reveal that there are strong cofacial interactions between the Pc side-chains. This is apparent from the large bathochromic shift of the primary Q-band of the Pc from 690 to 620 nm. We believe that these interactions are primarily intramolecular because even very dilute solutions show this effect, whereas solutions of monomer **4** or **5** of similar concentration display an unperturbed Q-band (Fig. 1). UV–VIS spectra of the copolymers also display the broad absorption band resulting from self-association. High resolution ^{1}H NMR spectroscopy clearly shows the presence of the dodecyloxy groups attached to the Pc side-chains, however the aromatic protons are indicated only by a single very broad signal centred at δ 6.9, presumably due to intramolecular association of the Pc units. NMR spectra of the copolymers show clear signals originating from the polystyrene backbone, however, only broadened resonances from the alkyl component of the Pc-containing side-chain are apparent. This

Table 1 Polymerisation data for Pc-containing styrenes prepared using the conditions described in the text. Each figure for conversion and M_n is an average of several runs.



Monomer(s)	x (%)	y (%)	Conversion (%)	$<M_n>$ (amu)	$<M_w>/<M_n>$
4	100	0	87	44×10^3	1.6
5	100	0	90	53×10^3	1.3
4 + styrene	0.5	99.5	95	72×10^3	1.7
5 + styrene	20	80	95	46×10^3	1.5
5 + styrene	0.5	99.5	94	80×10^3	1.7
Styrene + ODPc	0	100	89	8×10^3	1.7
Styrene + ZnODPc	0	100	90	10×10^3	1.7
Styrene	0	100	88	7×10^3	2.0

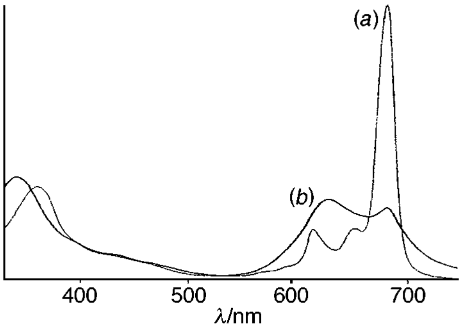


Fig. 1 UV–VIS absorption spectrum for (*a*) the monomer **5** and (*b*) the polystyrene derived from **5** (x = 100%).

observation reinforces the evidence from UV–VIS spectroscopy that Pc self-association is a feature of the dilute solution behaviour of the copolymers even for those which possess only a small degree of Pc side-chain substitution (~0.5 mol% concentration).

Unlike the precursors and monomers **2–5** which form a columnar mesophase at elevated temperatures, thin films of the Pc-containing homopolymers are birefringent solids up to their decomposition temperatures (~300 °C). The copolymers are isotropic glassy solids with well-defined glass transition temperatures. Thin films of the copolymers, fabricated by spin-coating or by melt processing, are optically clear and highly coloured. The non-scattering nature of these films make them suitable for optical studies.

This work illustrates the compatibility of Pc-containing styrene monomers with free radical polymerisation to produce well-defined macromolecules. It allows the design of novel, readily processed functional materials including polymeric dyes, polymer supported Pc-catalysts, photobactericidal polymers[12] and polymers for various optical applications.

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Notes and references

† *Selected data* for **4**: λ(toluene)/nm 700, 664, 646, 398, 342; ν(thin film)/cm^{-1} 3422 (NH); δ_H(benzene-d_6, 500 MHz, 60 °C) −3.40 (2H, br s), 0.99 (18H, t), 1.30–1.85 (108H, br m), 2.08–2.24 (12H, br m), 3.78 (2H, t), 4.24 (12H, br s), 4.40 (2H, br s), 5.06 (1H, d), 5.56 (2H, d), 6.64 (1H, dd), 6.85 (2H, d), 7.27 (2H, d), 7.68 (1H, br s), 8.30–8.70 (7H, br m), 9.12 (1H, br s); *m/z* (MALDI) 1906 (M$^+$). For **5**: λ(toluene)/nm 679, 612, 360; δ_H(benzene-d_6, 500 MHz, 60 °C) 1.01 (18H, t), 1.40–1.70 (96H, br m), 1.72–1.88 (12H, br m), 2.08–2.24 (12H, br m), 3.80 (2H, t), 4.12–4.26 (12H, br m), 4.36 (2H, br s), 5.06 (1H, d), 5.56 (2H, d), 6.64 (1H, dd), 6.85 (2H, d), 7.27 (2H, d), 7.65 (1H, br s), 8.15–8.65 (7H, br m), 9.12 (1H, br s); *m/z* (MALDI) 1971 (M$^+$).

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