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The synthesis and properties of vinyl substituted naphthopyrans and their styrene copolymers

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ABSTRACT

A comprehensive series of mono-, di- and tri-bromo-3*H*-naphtho[2,1-*b*]pyrans was synthesised by the traditional union of a 2-naphthol with an alkynol. The bromine atom(s) in these naphthopyrans was readily replaced by a vinyl group using a Suzuki coupling reaction with vinyl boronic anhydride pyridine complex. The efficiency of the Suzuki vinylation reaction decreases with the increasing number of bromine atoms to be substituted. The vinylnaphthopyrans served as styrene analogues and readily underwent a thermally initiated free radical addition co-polymerisation with styrene to efficiently afford low molecular weight poly(styrene-co-naphthopyrans).

The photochromic response of the bromonaphthopyrans and vinylnaphthopyrans followed the established colour-structure relationships for photochromic naphthopyrans. The photochromic response of toluene solutions of the poly(styrene-co-naphthopyrans) was characterised by a hypsochromic shift of the λ_{max} relative to that recorded for the vinylnaphthopyran monomers. Increased half-lives were noted for the copolymers derived from the bis- and tris-vinylnaphthopyrans where some degree of crosslinking was expected. A further hypsochromic shift in λ_{max} resulted for the thin films of the poly(styrene-co-naphthopyrans). Of particular note was the behaviour of the 3-(2-vinylphenyl)-3-phenylnaphthopyran which gave the typical yellow colour of the photomerocyanine coupled with the predictable large half-life. However, all photochromism of this naphthopyran was lost upon polymerisation suggesting that an alternative pathway supervenes in the expected polymerisation sequence.

1. Introduction

The commercial success of photochromic naphthopyrans, predominantly due to their incorporation in a variety of polymeric host materials for ophthalmic lens applications [1], has ensured a healthy interest in the design and synthesis of many new variants [2]. Naphthopyran structure–photochromic activity relationships, established by examining the photochromic response of structurally diverse compounds, are well documented for the angular naphthopyran isomers **1** and **2** (Scheme 1) [3].

Macromolecular chromophores have attracted steady interest over the last two decades and advances in this area have been reviewed [4]. Recently, this interest has extended to encompass polymeric and oligomeric photochromic naphthopyrans. The use of atom transfer radical polymerisation (ATRP) systems (CuBr/bipyridine), to introduce polyester chains of varying length and complexity onto photochromic macroinitiators **3** and **4** [5], **5** [6] and **6** [7] (Scheme 2), has enabled the efficient tuning of the half-life of the photomerocyanine; a key parameter of photochromic systems for ophthalmic applications.

Whilst reversible addition fragmentation chain transfer polymerisation (RAFT) has been employed with the sulphur containing RAFT agent, 2-(2-cyanopropyl)dithiobenzoate, to access various acrylate–naphthopyran copolymer systems, derived from acrylates of the type **7** and **8**. In these the photochromic switching speed was dependent upon the polymeric architecture (Scheme 3) [8]. In an elaboration of the foregoing studies, photochromic acrylate monomers of the type **9** have been copolymerised using the ATRP technique, with α-bromoisobutyryl esters that were derived from the esterification of hydroxyl-terminated poly(butadiene diol) with α-bromoisobutryl bromide. The resulting copolymers have elastic properties that may offer new applications for photochromic materials [9]. Durable photochromic organopolysiloxane coatings have been obtained through the platinum-catalysed hydrosilylation of the terminal vinylalkylnaphthopyran ethers **10** (Scheme 3) [10].

Following scrutiny of the literature that is associated with such photochromic naphthopyran polymers we were surprised to note

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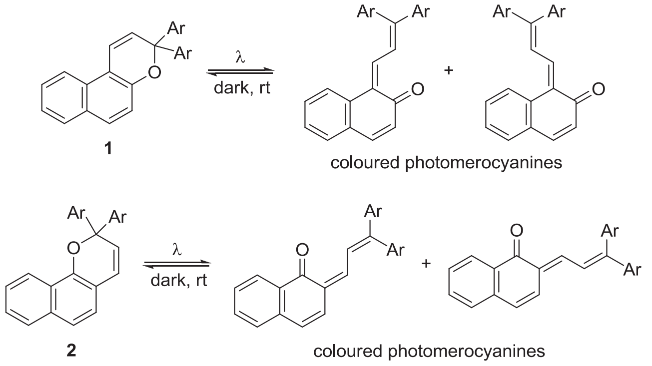
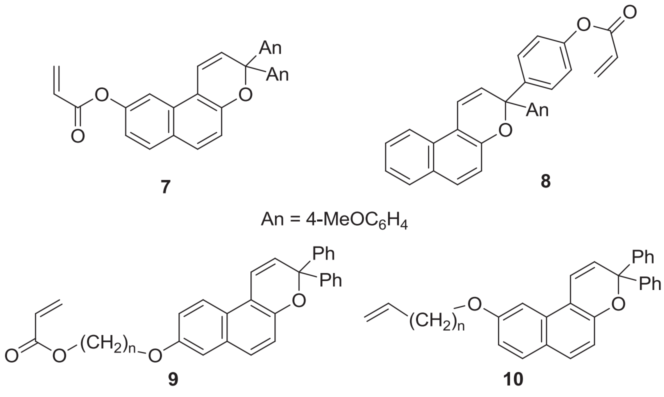


Scheme 1. Photoinduced ring-opening of the isomeric angular naphthopyrans **1** and **2**.



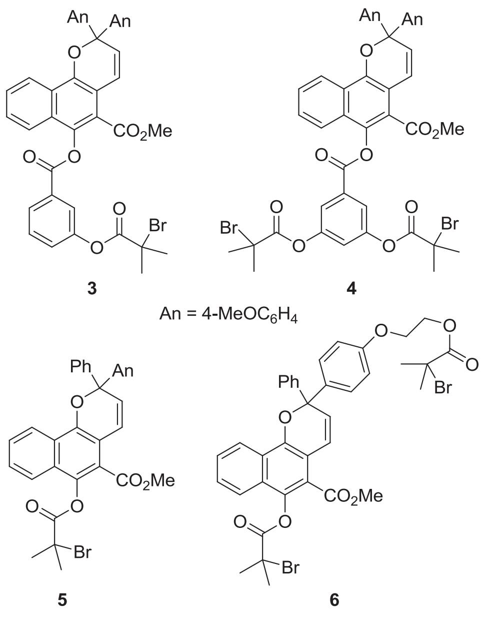
Scheme 3. Acrylate and vinyl substituted naphthopyran monomers.

that vinyl substituted naphthopyrans and their copolymerisation with styrene has not been investigated, in spite of the broad applications of poly(styrene) based systems. We now report our preliminary studies concerning the synthesis and simple free radical addition copolymerisation studies of a series on mono-, bis- and tris-vinyl substituted naphthopyrans.

2. Experimental

2.1. Equipment

Unless otherwise stated, reagents were used as supplied by the major chemical catalogue companies. The di-*t*-butylcatechol inhibitor was removed from styrene (Aldrich) by elution of the neat styrene through a short (40 mm depth, 40 mm diameter) basic alumina column; the resulting inhibitor-free styrene was stored in a refrigerator (+4 °C) and used within 1 h. NMR spectra were recorded using either a Bruker Avance 400 MHz spectrophotometer (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) or a Bruker Avance 500 MHz spectrophotometer (^{1}H NMR 500 MHz, ^{13}C NMR 125 MHz) for sample solutions in $CDCl_3$, with tetramethylsilane as an internal reference. Melting points and glass transition temperatures (T_g) were determined using a TA Instrument DSC 2010, run at 10 °C/min under N_2 (200 mL/min). The sample history was erased by a pre-heating (to 150 °C) and cooling cycle prior to the T_g data acquisition run. The number average molar mass (M_n), weight average molar mass (M_w) and polydispersity index (PDI) were determined using a size exclusion chromatography (SEC) system that was equipped with a LC1120 HPLC pump (Polymer Laboratories, UK), a differential refractive index (DRI) detector (Shodex, RI-101), a 5.0 μm bead-sized guard column (50 × 7.5 mm), and two PLgel 5.0 μm MIXED-C columns (300 × 7.5 mm) in series (Polymer Laboratories, UK). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1} at ambient temperature. Toluene was used as a flow marker. The SEC system was calibrated with poly(styrene) standards (Polymer Laboratories UK), the average molar mass of the standards ranging from 162 to 6,035,000 g mol^{-1}. FT-IR spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer system that was equipped with a golden gate ATR attachment (neat sample). UV–visible spectra were recorded for either spectroscopic grade PhMe solutions of the samples (10 mm pathlength quartz cuvette, PTFE capped, concentration in the range 1×10^{-4}–10^{-6} mol dm^{-3}) or in a thin film deposited on a microscope slide from a CH_2Cl_2 solution. A Cary 50 Probe spectrophotometer was used that was equipped with a single cell Peltier temperature controlled (20 °C) stirred cell attachment with activating irradiation provided by an Oriel 150 Watt xenon arc lamp source (Newport 66906), xenon ozone free arc lamp (Newport 6255), distilled water liquid filter (Newport 6177), multiple filter holder (Newport 62020), UG11 filter (Newport FSO-UG11), fibre optic coupler (Newport 77799) and liquid light guide (Newport 77557). Spectra (350–750 nm) were recorded prior to (ground state) and immediately after cessation of activating irradiation to a steady state (3 min irradiation), at given time intervals, over a period that was sufficient for decay of the photoinduced colour to revert to its initial coloration. All of the compounds were homogeneous as determined by TLC (Merck TLC aluminium sheets, silica gel 60 F_{254}), using a range of eluent systems of differing polarity. Flash column chromatography was performed on chromatography grade silica gel (Fluorochem, 40–63 μ particle size distribution). All the compound yields are unoptimised. High resolution mass spectra were recorded at the National EPSRC Mass Spectrometry Service Centre, Swansea using a Thermo Scientific LTQ Orbitrap XL Fourier transform mass spectrometer. 2-Bromobenzophenone (98% yield, mp 40–42 °C, lit. mp 42 °C [11]) and 3-bromobenzophenone (76% yield, mp 71–72 °C, lit. mp 78 °C [12]) were prepared by anhydrous aluminium chloride-mediated Friedel–Crafts acylation of benzene, according to literature protocols and had physical and spectroscopic properties comparable to those reported.



Scheme 2. Photochromic macroinitiators for ATRP.

2.2. Preparation of 1,1-diarylprop-2-yn-1-ols

n-Butyllithium (2.5 M in hexanes) (1.1 mol equiv) was added over 5 min with a syringe to a cold (+10 °C), stirred solution of trimethylsilylacetylene (1.1 mol equiv) in anhydrous tetrahydrofuran (200 mL) under nitrogen. On completion of the addition (*ca*. 5 min), the cold solution was stirred for 30 min. The benzophenone (1 mol equiv) was then added in a single portion. The cooling bath was removed and the mixture stirred until no benzophenone remained, as ascertained by TLC (typically *ca*. 3 h). The reaction mixture was then cooled to 0 °C and a solution of methanolic potassium hydroxide was added [from potassium hydroxide (2 mol equiv) in methanol (40 mL) in a single portion]. The cooling bath was then removed and the mixture warmed to room temperature. After *ca*. 15 min TLC indicated that the acetylene deprotection was complete. The mixture was poured into water (400 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (2 × 100 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave the 1,1-diaryl-prop-2-yn-1-ol, which, after routine ^{1}H NMR examination, was used directly for the preparation of the requisite bromonaphthopyran.

2.2.1. 1-(4-Bromophenyl)-1-phenylprop-2-yn-1-ol **11**

From 4-bromobenzophenone and isolated as off-white microcrystals (20.3 g, 92%) after recrystallisation from ethyl acetate and hexane, mp 79.9–80.7 °C (lit. mp 81 °C [13]), ν_{max} 3532, 3287, 1574, 1478 cm^{-1}, δ_H 2.75 (1H, s, alkyne-H), 2.88 (1H, s, OH), 7.30 (3H, m, Ar–H), 7.45 (4H, m, Ar–H), 7.57 (2H, m, Ar–H).

2.2.2. 1-(3-Bromophenyl)-1-phenylprop-2-yn-1-ol **12**

From 3-bromobenzophenone and isolated as a viscous pale brown oil which could not be induced to crystallise (10.8 g, 96%), (lit. mp 41 °C [14]), ν_{max} 3542, 3273, 1562, 1387, 1060 cm^{-1}, δ_H 2.89 (1H, s, alkyne-H), 2.98 (1H, bs, OH), 7.16 (1H, m, Ar–H), 7.30 (3H, m, Ar–H), 7.38 (1H, m, Ar–H), 7.49 (1H, m, Ar–H), 7.56 (2H, m, Ar–H), 7.79 (1H, s, Ar–H).

2.2.3. 1-(2-Bromophenyl)-1-phenylprop-2-yn-1-ol **13**

From 2-bromobenzophenone and isolated as pale brown solid (11.1 g, 99%), mp 52.8–53.2 °C (lit. mp 51 °C [14]), ν_{max} 3537, 3283, 1565, 1473, 811 cm^{-1}, δ_H 2.85 (1H, s, alkyne-H), 3.28 (1H, s, OH), 7.20 (1H, m, Ar–H), 7.33 (3H, m, Ar–H), 7.39 (1H, m, Ar–H), 7.50 (2H, m, Ar–H), 7.56 (1H, m, Ar–H), 8.01 (1H, dd, $J = 7.5$, 2.0 Hz, Ar–H).

2.2.4. 1,1-Bis(4-bromophenyl)prop-2-yn-1ol **14**

From 4,4-dibromobenzophenone and isolated as an off-white powder (14.4 g, 89%) mp 98.4–98.6 °C (lit. mp 100–101 °C [15]), ν_{max} 3551, 3282, 1572, 1478, 1395, 1065, 814 cm^{-1}, δ_H 2.75 (1H, s, alkyne-H), 2.89 (1H, s, OH), 7.42 (8H, m, Ar–H).

2.2.5. 1,1-Diphenylprop-2-yn-1-ol **15**

From benzophenone and isolated as a very pale yellow semisolid (21.7 g, 95%) that gradually solidified on standing to give a pale yellow solid, mp 43.1–45.4 °C, (lit. mp 47 °C [15]), ν_{max} 3426, 3283, 1597, 1489, 1448 cm^{-1}, δ_H 2.72 (1H, s, alkyne-H), 2.83 (1H, s, OH), 7.17 (6H, m, Ar–H), 7.47 (4H, m, Ar–H).

2.2.6. 1-(4-Biphenyl)-1-phenylprop-2-yn-1-ol **16**

From 4-phenylbenzophenone and isolated as a pale brown solid (5.4 g, 99%), mp 92.4–93.6 °C (lit. mp 95 °C [16]), ν_{max} 3541, 3280, 3060, 2116, 1952, 1809, 1634, 1486, 1447, 1200, 1163, 1003, 750, 693, 522 cm^{-1}, δ_H 2.82 (1H, s, alkyne-H), 2.88 (1H, s, OH), 7.35 (6H, m, Ar–H), 7.55 (4H, m, Ar–H), 7.65 (4H, m, Ar–H).

2.3. Preparation of simple and bromo substituted naphthopyrans

A solution of the 2-naphthol (1 mol equiv) and propargyl alcohol (1 mol equiv), in the presence of PPTS (5 mol %) and trimethyl orthoformate (2 mol equiv) in 1,2-dichloroethane (100 mL), was heated under reflux for up to 24 h (the reaction time being determined by TLC examination of the reaction mixture). The cooled solvent was removed under vacuum to afford a brown gum that was purified by flash column chromatography. The following compounds were obtained in this manner:

2.3.1. 3-(4-Bromophenyl)-3-phenyl-3H-naphtho[2,1-b]pyran **17**

From 2-naphthol and 1-(4-bromophenyl)-1-phenylprop-2-yn-1-ol, as an off-white powder after elution from silica using 5% dichloromethane in hexane, (11.1 g, 77%), mp 186.8–187.2 °C (lit. mp 183–184 °C [17]), ν_{max} 3058, 1484, 1003, 807 cm^{-1}, δ_H 6.19 (1H, d, $J = 9.9$ Hz, 2-H), 7.16 (1H, dd, $J = 0.4$, 8.9 Hz, 5-H), 7.25 (1H, m, Ar–H), 7.33 (6H, m, Ar–H), 7.45 (5H, m, Ar–H), 7.65 (1H, d, $J = 8.8$ Hz, 6-H), 7.71 (1H, d, $J = 8.1$ Hz, 7-H), 7.94 (1H, d, $J = 8.1$ Hz, 10-H).

2.3.2. 3-(3-Bromophenyl)-3-phenyl-3H-naphtho[2,1-b]pyran **18**

From 2-naphthol and 1-phenyl-1-(3-bromophenyl)prop-2-yn-1-ol, as a viscous pale brown oil after elution from silica with 2% ethyl acetate in toluene, (2.7 g, 27%), ν_{max} 3058, 1895, 1630, 1566, 1461, 1218, 1084, 1009, 807, 737, 692 cm^{-1}, δ_H 6.21 (1H, d, $J = 10$ Hz, 2-H), 7.19 (2H, m, Ar–H, 5-H), 7.28 (1H, m, Ar–H), 7.34 (3H, m, Ar–H), 7.39 (2H, m, Ar–H), 7.46 (2H, m, Ar–H), 7.54 (1H, m, Ar–H), 7.70 (4H, m, Ar–H, 6-H), 7.95 (1H, d, $J = 8.5$ Hz, 10-H). Found $[M + H]^+$ 413.0538; $C_{25}H_{17}BrO$ requires $[M + H]^+$ 413.0536.

2.3.3. 3-(2-Bromophenyl)-3-phenyl-3H-naphtho[2,1-b]pyran **19**

From 2-naphthol and 1-phenyl-1-(2-bromophenyl)prop-2-yn-1-ol, as a viscous oil after elution from silica with 2% ethyl acetate in toluene, (0.5 g, 5%), ν_{max} 3284, 3057, 3062, 1951, 1807, 1631, 1487, 1446, 1217, 1081, 1004, 807, 750, 726, 692 cm^{-1}, δ_H 6.50 (1H, d, $J = 10.0$ Hz, 2-H), 7.18 (3H, m, Ar–H), 7.30 (5H, m, Ar–H), 7.42 (1H, d, $J = 10.0$ Hz), 7.48 (2H, m, Ar–H), 7.55 (1H, d, $J = 8.5$ Hz, Ar–H), 7.65 (1H, d, $J = 8.8$ Hz, Ar–H), 7.72 (1H, d, $J = 8.1$ Hz, 7-H), 7.80 (1H, d, $J = 8.8$ Hz, 6-H), 7.95 (1H, d, $J = 8.5$ Hz, 10-H). Found $[M + H]^+$ 413.0538; $C_{25}H_{17}BrO$ requires $[M + H]^+$ 413.0536.

2.3.4. 8-Bromo-3,3-diphenyl-3H-naphtho[2,1-b]pyran **20**

From 6-bromo-2-naphthol and 1,1-diphenylprop-2-yn-1-ol as pale brown microcrystals after elution from silica using 2% ethyl acetate, 10% hexane and 88% toluene, (16.1 g, 81%), mp 149.6–150.4 °C, (lit. mp 148 °C [18]), ν_{max} 3026, 1445, 1211, 1005, 697 cm^{-1}, δ_H 6.28 (1H, d, $J = 10.0$ Hz, 2-H), 7.20 (1H, d, $J = 8.9$ Hz, 5-H), 7.24 (4H, m, Ar–H), 7.32 (4H, m, Ar–H), 7.47 (4H, m, Ar–H), 7.51 (1H, dd, $J = 2.1$, 8.9 Hz, 9-H), 7.55 (1H, d, $J = 8.8$ Hz, 6-H), 7.80 (1H, d, $J = 9.0$ Hz, 10-H), 7.85 (1H, d, $J = 2.0$ Hz, 7-H), δ_C 82.7, 114.14, 117.3, 119.1, 123.2, 127.0, 127.6, 128.1, 128.28, 128.33, 128.8, 129.8, 130.4, 130.5, 144.6, 150.8.

2.3.5. 3,3-Bis(4-bromophenyl)-3H-naphtho[2,1-b]pyran **21**

From 2-naphthol and 1,1-bis(4-bromophenyl)prop-2-yn-1-ol, as very pale brown microcrystals after elution from silica using 10% dichloromethane in hexane, (6.3 g, 78%), mp 219–220 °C, ν_{max} 3056, 1483, 1072, 1002, 952, 810 cm^{-1}, δ_H 6.14 (1H, d, $J = 9.9$ Hz, 2-H), 7.15 (1H, d, $J = 8.8$ Hz, 5-H), 7.34 (6H, m, Ar–H), 7.45 (5H, m, Ar–H), 7.66 (1H, d, $J = 8.9$ Hz, 6-H), 7.72 (1H, d, $J = 8.0$ Hz, 7-H), 7.94 (1H, d, $J = 8.4$ Hz, 10-H). Found $[M + H]^+$ 492.9623; $C_{25}H_{16}Br_2O$ requires $[M + H]^+$ 492.9620.

2.3.6. 8-Bromo-3-(4-bromophenyl)-3-phenyl-3H-naphtho[2,1-b]pyran **22**

From 6-bromo-2-naphthol and 1-(4-bromophenyl)-1-phenylprop-2-yn-1-ol, as off-white microcrystals after crystallisation from ethyl acetate and hexane, (7.8 g, 76%), mp 176–176.5 °C, ν_{max} 3056, 1909, 1753, 1628, 1580, 1483, 1210, 1069, 1002 cm^{-1}, δ_H 6.21 (1H, d, $J = 9.9$ Hz, 2-H), 7.18 (1H, d, $J = 8.9$ Hz, 5-H), 7.24 (1H, s, Ar–H), 7.77 (1H, m, Ar–H), 7.32 (3H, m, Ar–H), 7.35 (1H, m, Ar–H), 7.43 (4H, m, Ar–H), 7.52 (1H, dd, $J = 2.0$, 9.0 Hz, Ar–H), 7.55 (1H, d, $J = 8.8$ Hz, Ar–H), 7.80 (1H, d, $J = 9.1$ Hz, 10-H), 7.86 (1H, d, $J = 2.0$ Hz, 7-H). Found $[M + H]^+$ 492.9622; $C_{25}H_{16}Br_2O$ requires $[M + H]^+$ 492.9620.

2.3.7. 3,3-Bis(4-bromophenyl)-8-bromo-3H-naphtho[2,1-b]pyran **23**

From 6-bromo-2-naphthol and 1,1-bis(4-bromophenyl)prop-2-yn-1-ol, as beige microcrystals (7.2 g, 77%), mp 151.5–152 °C (lit. mp 152–153.5 °C [17]), $\nu_{max} = 3054$, 1910, 1749, 1629, 1579, 1482, 1180, 1069, 1003, 959, 816 cm^{-1}, δ_H (d_8-PhMe) 5.72 (1H, d, $J = 9.9$ Hz, 2-H), 6.82 (1H, d, $J = 9.7$ Hz, 5-H), 6.93 (1H, d, $J = 8.9$ Hz, 9-H), 7.09 (5H, m, Ar–H, 1-H), 7.20 (4H, m, Ar–H), 7.36 (2H, m, 6-H, 10-H), 7.57 (1H, d, $J = 1.8$ Hz, 7-H).

2.3.8. 3-(4-Biphenyl)-1-phenyl-3H-naphtho[2,1-b]pyran **24**

From 2-naphthol and 1-(1-biphenyl)-1-phenylprop-2-yn-1-ol, as pale brown microcrystals after recrystallisation from ethyl acetate and hexane, (6.4 g, 88%), mp 179.9–180.4 °C, ν_{max} 3057, 1953, 1807, 1633, 1486, 1199, 1003, 807, 750, 725, 691, 483 cm^{-1}, δ_H 6.30 (1H, d, $J = 10.0$ Hz, 2-H), 7.22 (1H, d, $J = 8.8$ Hz, 5-H), 7.31 (7H, m, Ar–H, 1-H), 7.40 (2H, m, Ar–H), 7.54 (7H, m, Ar–H), 7.56 (1H, m, Ar–H), 7.66 (1H, d, $J = 8.8$ Hz, 6-H), 7.71 (1H, d, $J = 8.4$ Hz, 7-H), 7.96 (1H, d, $J = 8.4$, 10-H). Found $[M + H]^+$ 411.1745; $C_{31}H_{22}O$ requires $[M + H]^+$ 411.1743.

2.3.9. 3,3-Diphenyl-3H-naphtho[2,1-b]pyran **25**

From 2-naphthol and 1,1-diphenylprop-2-yn-1-ol, as an off-white solid after elution from silica using 10% ethyl acetate in hexane, (3.1 g, 67%), mp 158.0–158.3 °C, (lit. mp 158–159 °C [17]), ν_{max} 3062, 1953, 1809, 1635, 1489, 1215, 1092, 1083, 1008, 804, 750, 726, 695 cm^{-1}, δ_H 6.26 (1H, d $J = 9.9$ Hz, 2-H), 7.19 (1H, d, $J = 8.8$ Hz, 5-H), 7.25 (2H, m, Ar-H), 7.29 (6H, m, Ar–H), 7.48 (5H, m, Ar–H), 7.65 (1H, d, $J = 8.8$ Hz, 6-H), 7.71 (1H, d, $J = 8.1$ Hz, 7-H), 7.95 (1H, d, $J = 8.2$ Hz, 10-H).

2.4. Preparation of monovinylnaphthopyrans by a Suzuki coupling protocol

The aryl halide (1 mol equiv) was dissolved in degassed DME (20 mL), treated with tetrakis (triphenylphosphine) palladium (0) (10 mol%), and stirred at room temperature under N_2 for 20 min. Potassium carbonate (1 mol equiv), degassed water (6 mL) and vinyl boronic anhydride pyridine complex (O'Shea's reagent [19,20]) (1 mol equiv) were added. The reaction was heated under reflux under N_2 for 20 h. The reaction mixture was cooled to ambient temperature, filtered through a short path of silica with ethyl acetate (50 mL) and then washed with water (100 mL). The organic layer was dried (anhydrous Na_2SO_4) and the solvent evaporated. The crude residue was purified by flash column chromatography.

2.4.1. 3-Phenyl-3-(4-vinylphenyl)-3H-naphtho[2,1-b]pyran **26**

From 3-(4-bromophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran as colourless microcrystals after elution from silica using 20% toluene in hexane, (0.7 g, 76%), mp 97.6–101 °C, ν_{max} 3063, 1853, 1630, 1510, 1222, 1080, 1006, 924, 807, 693, 540 cm^{-1}, δ_H 5.21 (1H, d, $J = 10.9$ Hz, vinyl-H), 5.70 (1H, d, $J = 17.6$ Hz, vinyl-H), 6.25 (1H, d, $J = 9.96$ Hz, 2-H), 6.66 (1H, dd, $J = 17.6$, 10.9 Hz, vinyl-H), 7.20 (1H, d, $J = 8.8$ Hz, 5-H), 7.31 (7H, m, Ar–H), 7.43 (5H, m, Ar–H), 7.65 (1H, d, $J = 8.8$ Hz, 6-H), 7.70 (1H, d, $J = 8.1$ Hz, 7-H), 7.95 (1H, d, $J = 8.5$ Hz, 10-H). Found $[M + H]^+$ 361.1594; $C_{27}H_{20}O$ requires $[M + H]^+$ 361.1587.

2.4.2. 3-Phenyl-3-(2-vinylphenyl)-3H-naphtho[2,1-b]pyran **28**

From 3-(2-bromophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran, as a viscous yellow oil after elution from silica with 10% ethyl acetate in hexane, (1.7 g, 50%), ν_{max} 3059, 2924, 1632, 1447, 1244, 1083, 1005, 743, 699 cm^{-1}, δ_H 5.27 (1H, dd, $J = 11.0$, 1.5 Hz, vinyl-H), 5.62 (1H, dd, $J = 17.0$, 1.5 Hz, vinyl-H), 6.15 (1H, d, $J = 10.0$ Hz, 2-H), 6.97 (1H, dd, $J = 17.3$, 11.0 Hz, vinyl-H), 7.21 (1H, d, $J = 9.0$ Hz, 5-H), 7.35 (8H, m, Ar–H), 7.50 (4H, m, Ar–H), 7.58 (1H, d, $J = 9.0$ Hz, 6-H), 7.68 (1H, d, $J = 8.6$ Hz, 7-H), 8.01 (1H, d, $J = 8.4$ Hz, 10-H). Found: $[M + H]^+$ 361.1584; $C_{27}H_{20}O$ requires $[M + H]^+$ 361.1587.

2.4.3. 3,3-Diphenyl-8-vinyl-3H-naphtho[2,1-b]pyran **29**

From 3,3-diphenyl-8-bromo-3*H*-naphtho[2,1-*b*]pyran, as colourless microcrystals (0.8 g, 89%), after elution from silica using 20% toluene in hexane, mp 124.0–126.1 °C, ν_{max} 3058, 3026, 1631, 1447, 1243, 1217, 1093, 1006, 734, 693 cm^{-1}, δ_H 5.27 (1H, d, $J = 10.9$ Hz, vinyl-H), 5.80 (1H, d, $J = 17.6$ Hz, vinyl-H), 6.27 (1H, d, $J = 10.0$ Hz, 2-H), 6.81 (1H, dd, $J = 17.6$, 10.9 Hz, vinyl-H), 7.17 (2H, m, Ar–H), 7.30 (6H, m, Ar–H), 7.48 (4H, m, Ar–H), 7.62 (3H, m, Ar–H), 7.90 (1H, d, $J = 9.2$ Hz, 10-H). Found $[M + H]^+$ 361.1595; $C_{27}H_{20}O$ requires $[M + H]^+$ 361.1587.

2.5. Preparation of bis- and tris-vinylnaphthopyrans by a Suzuki coupling protocol

The aryl halide (1 mol equiv) was dissolved in degassed DME (30 mL), treated with tetrakis (triphenylphosphine) palladium (0) (12 mol%), and stirred at room temperature under N_2 for 20 min. Potassium carbonate (2 [or 3] mol equiv[1]), degassed water (8 mL) and vinyl boronic anhydride pyridine complex (O'Shea's reagent) (2 [or 3] mol equiv) were added. The reaction was heated under reflux under N_2 for 20 h. The reaction mixture was cooled to ambient temperature, filtered through a short path of silica with ethyl acetate (50 mL) and then washed with water (100 mL). The organic layer was dried (anhydrous Na_2SO_4) and the solvent evaporated. The crude residue was purified by flash column chromatography.

2.5.1. 3,3-Bis(4-vinylphenyl)-3H-naphtho[2,1-b]pyran **30**

From 3,3-bis(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran, as colourless microcrystals after elution from silica using 20% toluene in hexane, (0.4 g, 50%), mp 114–114.5 °C, ν_{max} 2981, 1918, 1813, 1629, 1224, 1084, 986, 903, 828 cm^{-1}, δ_H 5.22 (2H, dd, $J = 0.8$, 10.9 Hz, vinyl-H), 5.70 (2H, dd, $J = 0.8$, 17.6 Hz, vinyl-H), 6.23 (1H, d, $J = 9.9$ Hz, vinyl-H), 6.68 (2H, dd, $J = 17.6$, 10.9 Hz, vinyl-H), 7.19 (1H, d, $J = 8.8$ Hz), 7.32 (6H, m, Ar–H), 7.45 (4H, m, Ar–H), 7.65 (1H, d, $J = 8.8$ Hz), 7.70 (1H, d, $J = 8.1$ Hz), 7.95 (1H, d, $J = 8.4$ Hz, 10-H). Found $[M + H]^+$ 387.1739; $C_{29}H_{22}O$ requires $[M + H]^+$ 387.1743.

2.5.2. 3-Phenyl-8-vinyl-3-(4-vinylphenyl)-3H-naphtho[2,1-b]pyran **31**

From 8-bromo-3-(4-bromophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran as off-white microcrystals after elution from silica using 20% toluene in hexane, (0.3 g, 34%), mp = 117.2–118.1 °C, ν_{max} 3062, 1919, 1819, 1630, 1447, 1219, 1092, 1004, 985, 802, 731, 696 cm^{-1}, δ_H

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[1] Bis-vinylation employed 2 equivalents of K_2CO_3 and O'Shea's reagent and tris-vinylation required 3 equivalents of K_2CO_3 and O'Shea's reagent, respectively.

5.21 (1H, d, J = 10.9 Hz, vinyl-H), 5.27 (1H, d, J = 10.9 Hz, vinyl-H′), 5.70 (1H, d, J = 17.6 Hz, vinyl-H), 5.79 (1H, d, J = 17.6 Hz, vinyl-H′), 6.23 (1H, d, J = 9.9 Hz, 2-H), 6.66 (1H, dd, J = 17.6, 10.9 Hz, vinyl-H), 6.80 (1H, dd, J = 17.6, 10.9 Hz, vinyl-H′), 7.16 (1H, d, J = 8.8 Hz), 7.27 (5H, m, Ar—H), 7.43 (4H, m, Ar—H), 7.58 (3H, m, Ar—H), 7.87 (1H, d, J = 9.1 Hz, 10-H). Found $[M + H]^+$ 387.1753; $C_{29}H_{22}O$ requires $[M + H]^+$ 387.1743.

2.5.3. 8-Vinyl-3,3-bis(4-vinylphenyl)-3H-naphtho[2,1-b]pyran **32**

From 8-bromo-3,3-bis(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran, as an off-white amorphous powder after elution from silica using 20% toluene in hexane, (0.1 g, 14%), mp 136.0–137.5 °C, ν_{max} 2981, 1918, 1814, 1629, 1224, 1084, 986, 903, 828 cm^{-1}, δ_H 5.21 (2H, dd, J = 10.9, 0.8 Hz, vinyl-H), 5.26 (2H, dd, J = 10.9, 0.8 Hz, vinyl-H′), 5.70 (2H, dd, J = 17.6, 0.8 Hz, vinyl-H′), 5.80 (1H, dd, J = 17.6, 0.8 Hz, vinyl-H), 6.23 (1H, d, J = 9.9 Hz, 2-H), 6.67 (2H, dd, J = 17.6, 10.9 Hz, vinyl-H′), 6.82 (1H, dd, J = 17.6, 10.9 Hz, vinyl-H), 7.16 (1H, d, J = 8.9 Hz), 7.29 (1H, d, J = 9.9 Hz, 10-H). Found $[M + H]^+$ 413.1907; $C_{31}H_{24}O$ requires $[M + H]^+$ 413.1900.

2.6. Preparation of 3-phenyl-3-(4′-vinylbiphenyl-4-yl)-3H-naphtho[2,1-b]pyran 33 by a Suzuki coupling protocol

3-(4-Bromophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran **17** (1 mol equiv) was dissolved in degassed DME (20 mL), treated with tetrakis (triphenylphosphine) palladium (0) (10 mol%), and stirred at room temperature under N_2 for 20 min. Potassium carbonate (1 mol equiv), degassed water (6 mL) and 4-vinylbenzeneboronic acid (1 mol equiv) were added. The reaction was heated under reflux under N_2 for 20 h. The reaction mixture was cooled to ambient temperature, filtered through a short path of silica with ethyl acetate (50 mL) and then washed with water (100 mL). The organic layer was dried (anhydrous Na_2SO_4) and the solvent evaporated. Recrystallisation of the crude residue from ethyl acetate and hexane gave the title compound **33** as pale yellow microcrystals (1.97 g, 99%), mp = 193.5–195.0 °C, ν_{max} 3058, 1629, 1494, 1215, 1080, 1000, 807, 727, 693 cm^{-1}, δ_H 5.25 (1H, d, J = 11.0 Hz, vinyl-H), 5.76 (1H, d, J = 17.8 Hz, vinyl-H), 6.29 (1H, d, J = 10 Hz, 2-H), 6.72 (1H, dd, J = 17.8, 11.0 Hz, vinyl-H), 7.20 (4H, m, Ar—H), 7.34 (3H, m, Ar—H), 7.52 (10H, m, Ar—H), 7.66 (1H, d, J = 9.0 Hz, 6-H), 7.70 (1H, d, J = 8.5 Hz, 7-H), 7.95 (1H, d, J = 8.5 Hz, 10-H). Found: $[M + H]^+$ 437.1899; $C_{33}H_{24}O$ requires $[M + H]^+$ 437.1900.

2.7. Preparation of vinylbenzophenones

The bromobenzophenone (1 mol equiv) was dissolved in degassed DME (20 mL), treated with tetrakis (triphenylphosphine) palladium (0) (10 mol%), and stirred at room temperature under N_2 for 20 min. Potassium carbonate (1 mol equiv), degassed water (6 mL) and vinyl boronic anhydride pyridine complex (O'Shea's reagent) (1 mol equiv) were added. The reaction was heated under reflux under N_2 for 20 h. The reaction mixture was cooled to ambient temperature, filtered through a short path of silica with ethyl acetate (50 mL) and then washed with water (100 mL). The organic layer was dried (anhydrous Na_2SO_4) and the solvent evaporated. The crude residue was eluted from silica using 10% ethyl acetate in hexane, to afford the requisite vinylbenzophenone.

2.7.1. 4-Vinylbenzophenone **34a**

From 4-bromobenzophenone as a pale yellow solid (1.5 g 93%) mp softens *ca.* 53 °C, melt 61.0–62.8 °C, (lit. mp 51–52 °C [21]), ν_{max} = 3058, 2917, 1651, 1598, 1314, 1275, 923, 696 cm^{-1}, δ_H 5.38 (1H, d, J = 10.9 Hz, vinyl-H), 5.88 (1H, d, J = 17.6 Hz, vinyl-H), 6.77 (1H, dd, J = 10.9, 17.6 Hz, vinyl-H), 7.47 (4H, m, Ar—H), 7.56 (1H, m, Ar—H), 7.77 (4H, m, Ar—H). This material was used directly for the preparation of the requisite alkynol.

2.7.2. 3-Vinylbenzophenone **34b**

From 3-bromobenzophenone as a mobile yellow oil, (10.9 g, 99%), ν_{max} = 3058, 1967, 1655, 1595, 1447, 1275, 1204, 910, 693 cm^{-1}, δ_H 5.31 (1H, d, J = 11.0 Hz, vinyl-H), 5.79 (1H, d, J = 17.5 Hz, vinyl-H), 6.74 (1H, dd, J = 11.0, 17.5 Hz, vinyl-H), 7.46 (3H, m, Ar—H), 7.61 (3H, m, Ar—H), 7.82 (3H, m, Ar—H). This material was used directly for the preparation of the requisite alkynol.

2.8. Preparation of 1-phenyl-1-(4-vinylphenyl)prop-2-yn-1-ol **35a**

n-Butyllithium (2.5 M in hexanes) (1.1 mol equiv) was added slowly with a syringe to a cold (+10 °C), stirred solution of trimethylsilylacetylene (1.1 mol equiv), in anhydrous tetrahydrofuran (75 mL), under nitrogen. On completion of the addition (*ca.* 5 min) the cold solution was stirred for 30 min. 4-Vinylbenzophenone **34a** (1 mol equiv) was then added in a single portion, the cooling bath was removed and the mixture stirred until no 4-vinylbenzophenone remained as ascertained by TLC (typically *ca.* 3 h). The reaction mixture was then cooled to 0 °C and a solution of methanolic potassium hydroxide was added [from potassium hydroxide (2 mol equiv) in methanol (20 mL)] in a single portion. The cooling bath was then removed and the mixture warmed to room temperature, after *ca.* 15 min. TLC indicated that the acetylene deprotection was complete. The mixture was poured into water (200 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (2 × 500 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave the title compound **35a** as a pale brown oil (1.4 g, 99%), ν_{max} 3401, 3285, 3061, 2115, 1630, 1600, 1489, 1448, 986, 838, 697 cm^{-1}, δ_H 2.76 (1H, s, alkyne-H), 2.87 (1H, s, OH), 5.24 (1H, d, J = 10.9 Hz, vinyl-H), 5.73 (1H, d, J = 17.6 Hz, vinyl-H), 6.69 (1H, dd, J = 17.6, 10.9 Hz, vinyl-H), 7.32 (5H, m, Ar—H), 7.59 (4H, m, Ar—H). This material was used directly for the preparation of 3-phenyl-8-vinyl-3-(4-vinylphenyl)-3*H*-naphtho[2,1-*b*]pyran **31**.

2.9. Preparation of vinylnaphthopyrans from naphthols and vinyl substituted prop-2-yn-1-ols

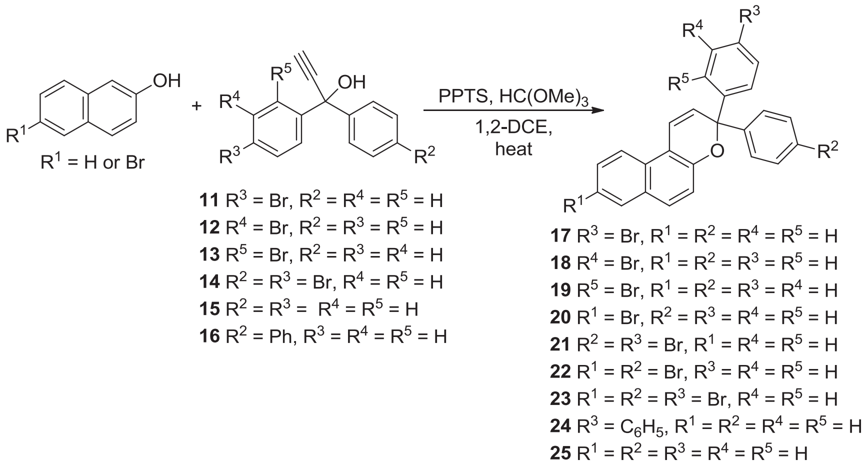
A solution of the 2-naphthol (1 mol equiv) and the vinyl substituted prop-2-yn-1-ol (1 mol equiv) in the presence of PPTS (5 mol%) and trimethyl orthoformate (2 mol equiv) in 1,2-dichloroethane (50 mL) was heated under reflux for up to 24 h (reaction time determined by TLC examination of the reaction mixture). The cooled solvent was removed under vacuum to afford a brown gum that was purified by flash column chromatography. The following compounds were obtained in this manner:

2.9.1. 3-Phenyl-8-vinyl-3-(4-vinylphenyl)-3H-naphtho[2,1-b]pyran **31**

From 6-vinyl-2-naphthol [22] and 1-phenyl-1-(4-vinylphenyl)prop-2-yn-1-ol **35a** as off-white microcrystals after elution from silica using 20% toluene in hexane, (0.48 g, 28%). The compound was identical in all aspects to that prepared previously by the Suzuki coupling protocol (Section 2.5.2).

2.9.2. 3-Phenyl-3-(3-vinylphenyl)-3H-naphtho [2,1-b]pyran **27**

From 2-naphthol and crude 1-phenyl-1-(3-vinylphenyl)prop-2-yn-1-ol **35b**, as a pale yellow solid after elution from silica using 50% toluene in hexane, (3.6 g, 39%), ν_{max} 3057, 1810, 1631, 1460, 1235, 1082, 1007, 799, 729, 695, δ_H 5.20 (1H, dd, J = 10.9, 0.6 Hz, vinyl-H), 5.69 (1H, dd, J = 17.8, 0.6 Hz, vinyl-H), 6.26 (1H, d,



Scheme 4. Synthesis of bromonaphthopyrans.

$J = 10.0$ Hz, 2-H), 6.67 (1H, dd, $J = 17.8, 10.9$ Hz, vinyl-H), 7.20 (1H, d, $J = 9.0$ Hz, 5-H), 7.30 (8H, m, Ar–H, 1-H), 7.43 (3H, m, Ar–H), 7.54 (1H, s, Ar–H), 7.65 (1H, d, $J = 8.5$ Hz, 6-H[2]), 7.70 (1H, d, $J = 8.5$ Hz, 7-H[2]), 7.95 (1H, d, $J = 8.5$ Hz, 10-H). Found $[M + H]^+$ 361.1586; $C_{27}H_{20}O$ requires $[M + H]^+$ 361.1587.

2.10. General method for the polymerisation of the vinylnaphthopyrans

1,1′-Azobis(cyclohexanecarbonitrile) (0.1 mol equiv.) was added to a stirred solution of inhibitor free styrene (1.0 mol equiv.) and the vinylnaphthopyran (0.1 mol equiv.) in degassed (N_2 for 20 min) toluene (50 mL) under N_2 in a 100 mL three-neck round-bottom flask. The reaction mixture was heated at 100–110 °C for 6 h then stirred and cooled overnight. The reaction solution was added dropwise to cold methanol (250 mL, ~5 °C) over ~10 min and the resulting pale yellow suspension stirred for 2 h. The resulting pale yellow oligomer/polymer was collected by vacuum filtration, washed with ice cold methanol and air dried to a constant weight. The following compounds were obtained in this manner:

2.10.1. Poly(styrene-co-3,3-diphenyl-8-vinyl-3H-naphtho[2,1-b]pyran) *36* from *29*

As a pale yellow solid (4.18 g, 78%), $T_g = 80$ °C, $M_n = 2500$ g mol^{-1}, $M_w = 3887$ g mol^{-1}, PDI = 1.5548.

2.10.2. Poly(styrene-co-3-phenyl-3-(4-vinylphenyl)-3H-naphtho[2,1-b]pyran) *37* from *26*

As a pale yellow solid (5.34 g, 99%), $T_g = 74$ °C, $M_n = 2286$ g mol^{-1}, $M_w = 3769$ g mol^{-1}, PDI = 1.6487.

2.10.3. Poly(styrene-co-3-phenyl-3-(3-vinylphenyl)-3H-naphtho[2,1-b]pyran) *38* from *27*

As a pale yellow solid (4.05 g, 75%), $T_g = 70$ °C, $M_n = 2122$ g mol^{-1}, $M_w = 3039$ g mol^{-1}, PDI = 1.4321.

2.10.4. Poly(styrene-co-3-phenyl-3-(2-vinylphenyl)-3H-naphtho[2,1-b]pyran) *39* from *28*

As a yellow solid (3.92 g, 73%), $T_g = 87$ °C, $M_n = 2187$ g mol^{-1}, $M_w = 3192$ g mol^{-1}, PDI = 1.4595.

2.10.5. Poly(styrene-co-3,3-bis(4-vinylphenyl)-3H-naphtho[2,1-b]pyran) *40* from *30*

As a pale yellow solid (4.56 g, 84%), $T_g = 86$ °C, $M_n = 3153$ g mol^{-1}, $M_w = 5922$ g mol^{-1}, PDI = 1.8782.

2.10.6. Poly(styrene-co-3-phenyl-8-vinyl-3-(4-vinylphenyl)-3H-naphtho[2,1-b]pyran) *41* from *31*

As a pale yellow solid (2.07 g, 92%), $T_g = 80$ °C, $M_n = 3026$ g mol^{-1}, $M_w = 5536$ g mol^{-1}, PDI = 1.8295.

2.10.7. Poly(styrene-co-8-vinyl-3,3-bis(4-vinylphenyl)-3H-naphtho[2,1-b]pyran) *42* from *32*

As a pale yellow solid (4.59 g, 85%), $T_g = 87$ °C, $M_n = 2908$ g mol^{-1}, $M_w = 6583$ g mol^{-1}, PDI = 2.2638.

2.10.8. Poly(styrene-co-3-phenyl-4-(4′-vinylbiphenyl-4-yl)-3H-naphtho[2,1-b]pyran) *43* from *33*

As a pale yellow solid (4.95 g, 91%), $T_g = 78$ °C, $M_n = 2378$ g mol^{-1}, $M_w = 3645$ g mol^{-1}, PDI = 1.5328.

3. Discussion

3.1. Preparation of bromo- and vinyl-substituted naphthopyrans

The main strategy employed to access the vinyl substituted naphthopyrans that were required for the present study relied upon preparation of a series of mono-, di- and tri-bromo substituted 3*H*-naphtho[2,1-*b*]pyrans using the established reaction between a 1,1-diarylprop-2-yn-1-ol and a 2-naphthol [3,23]. It was realised that the vinyl group could then be introduced directly, under relatively mild conditions, using a Suzuki coupling protocol [24] with vinyl boronic anhydride pyridine complex (O'Shea's reagent) [20].

Examination of the literature revealed that only three of the required bromonaphthopyrans had been previously reported and were generally accessed in good yield; **17** and **23** [17] and **20** [18].

Whilst 4-bromo- and 4,4-dibromo-benzophenones are commercially available, the 2- [11] and 3-bromobenzophenones [12] were readily synthesised by traditional Friedel–Crafts acylation of benzene, in 98% and 76% yield, respectively. Addition of the bromobenzophenones to trimethylsilylacetylide, from *n*-butyllithium and trimethylsilylacetylene, gave the required mono-bromo- **11**–**13** and dibromo-propynols **14** in excellent yields. These compounds were used directly in the preparation of the naphthopyrans **17**–**23** (Scheme 4), according to the method devised by

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[2] Assignments may be reversed.

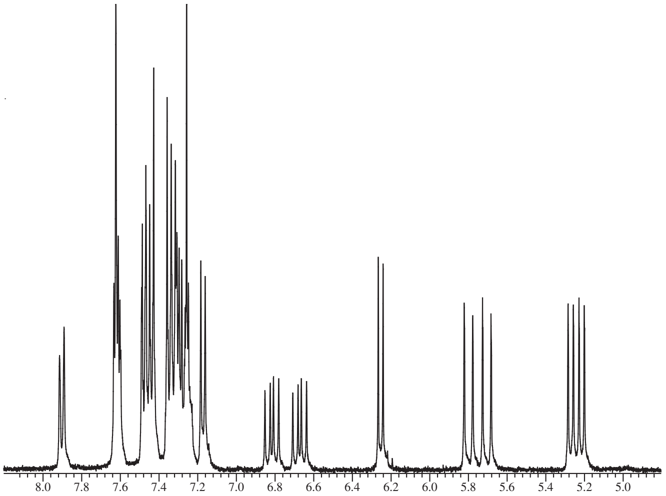


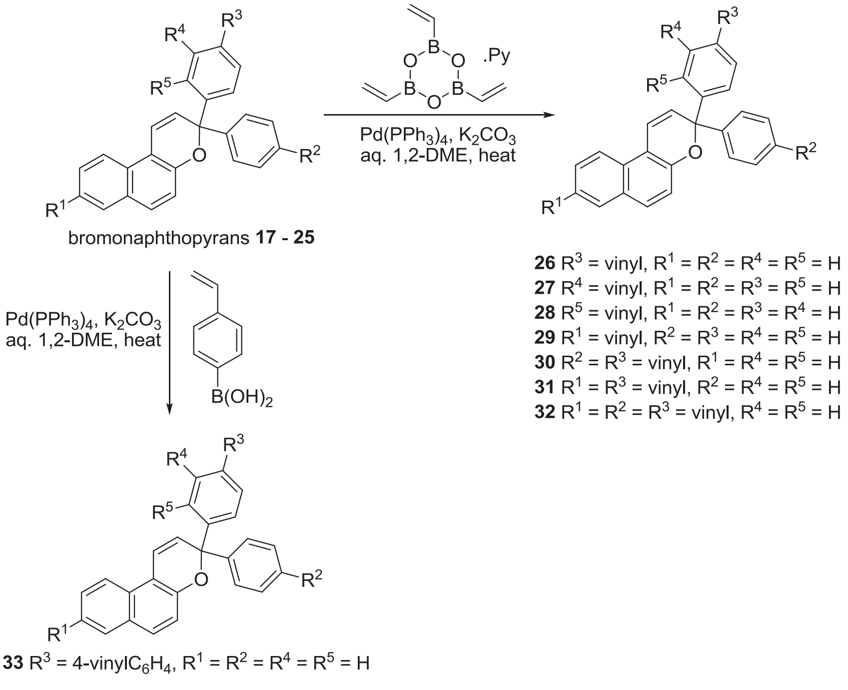
Fig. 1. ^{1}H NMR spectrum of divinylnapthopyran **31**.

Carreira et al., which employs pyridinium *p*-toluenesulfonate (PPTS) and trimethyl orthoformate in 1,2-dichloroethane [25]. Propynols **15** and **16** were obtained in 95 and 99% yield from benzophenone and 4-phenylbenzophenone, respectively. Reaction of **15** and **16** with 2-naphthol afforded the reference compounds **24** and **25**, respectively. The formation of the naphthopyran unit was confirmed by ^{1}H NMR spectroscopy which gave the expected doublet at δ 6.1–6.3 in $CDCl_3$ (ca. δ 5.7 d_8-PhMe) for 2-H with a *ca.* 10 Hz coupling constant; 1-H typically resonates at *ca.* δ 7.3–7.5 and is obscured by other aromatic signals [3,26].

With the series of bromonaphthopyrans obtained, their Suzuki coupling reaction with vinyl boronic anhydride pyridine complex (O'Shea's reagent) was explored. Thus, heating a solution of **17** with O'Shea's reagent in degassed aqueous 1,2-dimethoxyethane containing $Pd(PPh_3)_4$ and K_2CO_3 gave, after work-up, the 3-(4-vinylphenyl)naphthopyran **26** in 76% yield. ^{1}H NMR spectroscopy provided evidence for the incorporation of the vinyl moiety with the expected signals at δ 5.21(d, J = 10.9 Hz), δ 5.70 (d, J = 17.6 Hz) and δ 6.67 (dd, J = 17.6, 10.9 Hz) and the presence of the pyran ring was confirmed by the expected doublet at δ (2-H, d, J = 10.0 Hz). This latter point is noteworthy in view of recent reports of the ring-contraction of the pyran unit to a furan during palladium mediated reactions [27].

Following the success of this simple coupling protocol, the isomeric monovinyl substituted naphthopyrans **28** and **29** were similarly obtained. The location of the vinyl group, i.e. either attached to the naphthalene moiety at C-8 (viz. **29**) or on one of the C-3 aryl rings, could be established by ^{1}H NMR spectroscopy with the signals of the former resonating slightly downfield of those of the latter. The Suzuki coupling protocol was extended, with appropriate increases to the ratio of reactants, to the dibromo- **21** and **22** and tribromo-naphthopyrans **23**, to afford the poly(vinyl-substituted naphthopyrans) **30**–**32** in moderate yield. It should be noted that the yield of the trivinyl compound **32** was particularly low (14%) as a consequence of poor conversion that resulted in mixtures of mono-, di- and the target tri-vinyl compounds, which were not readily resolved by column chromatography. Furthermore, the formation of some polymeric material, of unspecified constitution, was noted from this reaction and presumably results from the ample opportunities presented for polymerisation of the three vinyl units. The ^{1}H NMR spectrum of the bis-vinylnaphthopyran **31** (Fig. 1) clearly shows the differentiation between the naphthylvinyl groups and the phenylvinyl groups.

The 3-phenyl-3-(3-vinylphenyl)naphthopyran **27** was not readily obtained by the foregoing coupling protocol. Therefore, an alternative strategy was adopted wherein O'Shea's reagent was coupled to 3-bromobenzophenone, using conditions that were identical to those employed for the coupling to bromonaphthopyrans, to afford 3-vinylbenzophenone **34b** in 99% yield (Scheme 6). Transformation of **34b** into naphthopyran **27** was accomplished in two steps in 39% yield without isolation of the intermediate vinylpropynol **35b**. A contributing factor to the moderate yield for this transformation is the formation of some intractable polymeric



Scheme 5. Synthesis of vinyl substituted naphthopyrans.

material in the pyran forming reaction, through the extended heating of the vinylpropynol. As a direct comparison between the Suzuki vinylation protocol of a bromonaphthopyran and the alternative reaction between a vinylpropynol and a vinylnaphthol, 6-vinyl-2-naphthol and vinylpropynol **35a**, derived from the direct vinylation of 4-bromobenzophenone with O'Shea's reagent, according to our general procedure, with subsequent addition of lithium trimethylsilylacetylide and desilylation (92% from 4-bromobenzophenone), were heated together in 1,2-DCE containing PPTS and $(MeO)_3CH$ to afford the bis-vinylnaphthopyran **31** in 28% yield, some 6% lower than the direct vinylation route to **31**. These two complementary routes have comparable efficiencies (~27%) and indicate the problems that increasing the number of vinyl groups has on the efficiency of vinylnaphthopyran formation.

The 3-(vinylbiphenyl)naphthopyran **33** was obtained in 99% yield through the related Suzuki coupling reaction of commercial 4-vinylphenylboronic acid with the bromobenzopyran **17** (Scheme 5).

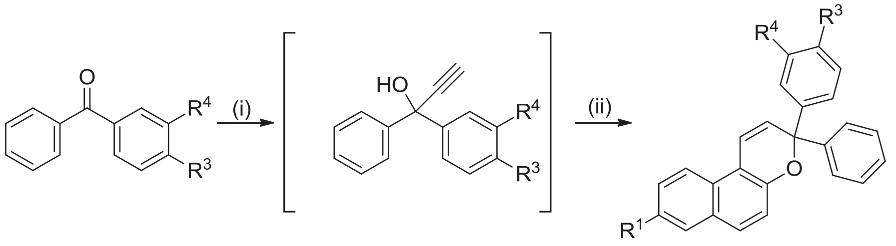
3.2. Free radical addition polymerisation of vinylnaphthopyrans

The polymerisation of the vinyl-substituted naphthopyrans was next explored. A "simple" free radical addition copolymerisation of the respective vinyl-substituted naphthopyrans with styrene was investigated in order to obtain preliminary data concerning the polymerisation of this series of novel vinylnaphthopyrans. A ratio of 1 mol equivalent of styrene, containing 0.1 mol equivalent of the vinylnaphthopyran, in degassed toluene employing 0.1 mol equivalent of 1,1′-azobis(cyclohexanecarbonitrile) (ACCN) as the thermal initiator was employed [28]. The reaction mixture was heated at ca. 110 °C for 6 h with stirring and then cooled overnight before precipitation of the product from cold methanol (~5 °C) and subsequent washing with cold methanol. TLC examination of the dried polymers in a variety of solvents indicated that no vinylnaphthopyran monomer remained. The polymers (Schemes 7 and 8) were obtained in high yield >73% as pale yellow solids with glass transition temperatures (T_g) in the range 70–87 °C. For the polymers **36**–**39** and **43**, derived from the monovinyl substituted naphthopyrans **26**–**29** and **33**, the number average molar masses (M_n) were in the range 2122–2500 g mol^{-1} and the weight average molar masses (M_w) were 3039–3887 g mol^{-1} with polydispersity indices (PDI) grouped between 1.65 and 1.43, indicating that some ordering took place in the polymerisation reaction pathway, giving such reasonably narrow molar mass distributions. The polymerisation of the bis-vinylnaphthopyrans **30** and **31** resulted in polymers **40** and **41** with greater M_n (3026–3153 g mol^{-1}) and M_w (5536–5922 g mol^{-1}) values coupled with deterioration in the PDI to ca. 1.85. The polymerisation of the tris-vinylnaphthopyran **32** resulted in **42** with the highest PDI of 2.26, with a M_n of 2908 g mol^{-1} and a M_w of 6583 g mol^{-1}. These data indicate that given a relatively high initiator concentration, low molecular weight styrene – vinylnaphthopyran polymers (oligomers) can be successfully prepared by a "simple" polymerisation protocol in which residual monomer is not a feature. Examination of the influence of decreasing the initiator concentration on the polymerisation processes is ongoing.

3.3. Photochromic properties of bromo- and vinyl-naphthopyrans

Toluene solutions of the bromo- and vinyl-naphthopyrans were irradiated to a steady state with an ultraviolet source (Section 2.1) in order to examine their photochromic properties. The photochromic response of the parent 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran **25** and the phenyl analogue **24** were recorded for comparison purposes. The wavelength of maximum absorption (λ_{max}) and the half-life ($t_{½}$) of the photomerocyanines are presented (Table 1). All of the bromonaphthopyrans that were synthesised developed a yellow–orange shade upon activation with UV irradiation, which generally faded quickly to the original state upon cessation of irradiation.

Introduction of bromine at the *p*-position of one of the C-3 phenyl rings (**17**) induces a marginal hypsochromic shift of λ_{max} with a negligible influence on $t_{½}$ relative to **25**. The incorporation of a second bromine atom in the *p*-position of the remaining phenyl ring, to afford **21**, results in maxima at 426 nm coupled with a marginally shorter half-life relative to the half-life of **25** and **17**. This is a feature that is in accord with established colour–structure relationships for photochromic naphthopyrans [3]. The placement of a bromine atom in the *m*-position of one of the C-3 phenyl rings (**18**) results in a hypsochromic shift in λ_{max} relative to **25**. The greatest hypsochromic shift in λ_{max} was noted for the *o*-bromo substituted analogue **19**. This shift of 12 nm cf. **25** was also accompanied by the largest $t_{½}$ of 417 s (Fig. 2). For **19**, the steric demand of the bulky bromine atom results in exceptionally poor orbital overlap of the bromophenyl ring, which may be considered to be approaching a near orthogonal arrangement with the remainder of the chromophore of the photomerocyanine. This arrangement effectively insulates the chromophore from the bromophenyl unit, resulting in the observed hypsochromic shift. The increase in $t_{½}$ is a consequence of the twisted bromophenyl unit, hindering the usually rapid thermal cyclisation to the colourless naphthopyran. The influence of the size of the *o*-substituent in a C-3 aryl group upon the photochromism of 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans has been previously noted [3,29].



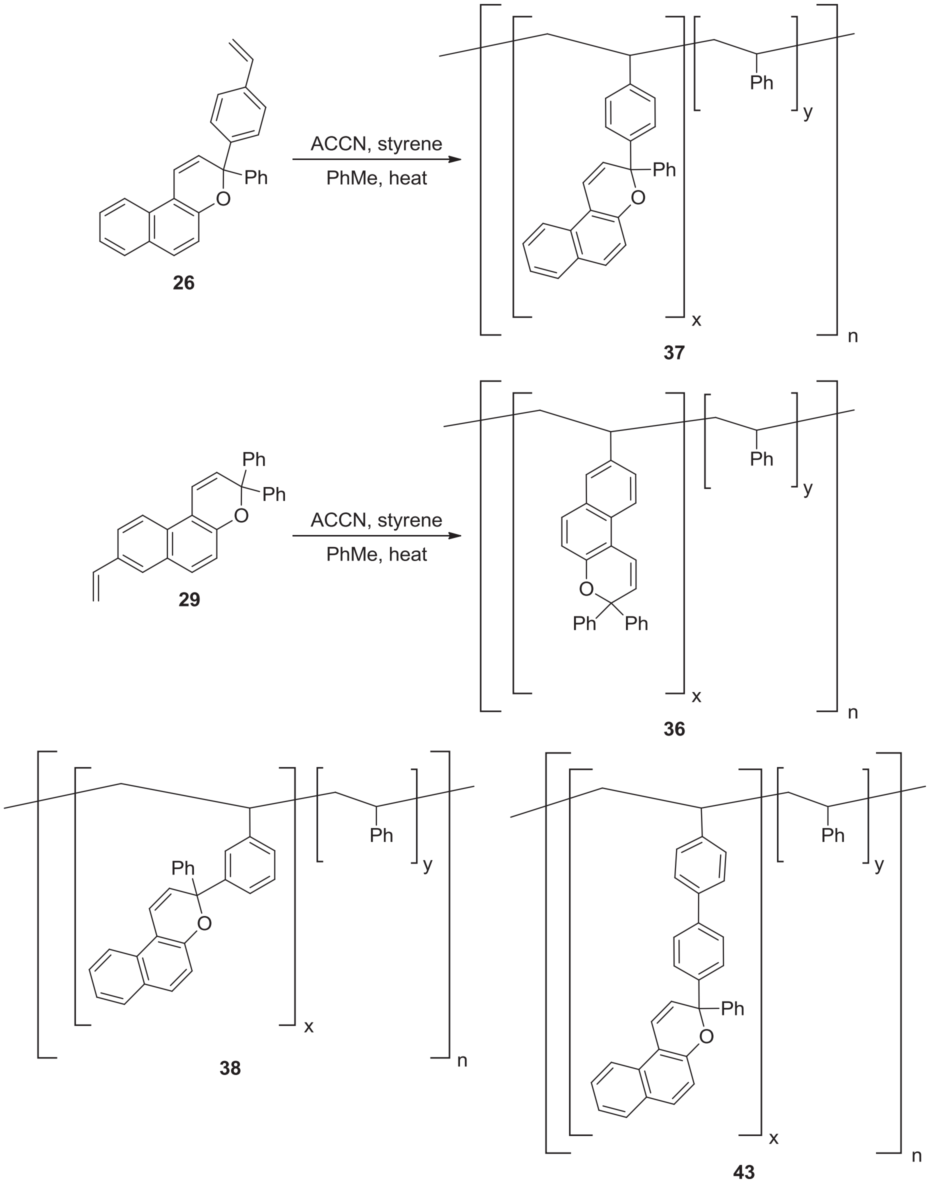
34a R^3 = vinyl, R^4 = H
34b R^3 = H, R^4 = vinyl

35a R^3 = vinyl, R^4 = H
35b R^3 = H, R^4 = vinyl

31 R^1 = R^3 = vinyl, R^4 = H
27 R^1 = R^3 = H, R^4 = vinyl

Reagents: (i) trimethylsilyacetylide, THF 0 °C - rt then methanolic KOH;
(ii) 2-naphthol or 6-vinyl-2-naphthol, PPTS, $(MeO)_3CH$, 1,2-DCE, heat

Scheme 6. Alternative method for the preparation of vinylnaphthopyrans.



Scheme 7. Preparation of Poly(styrene-co-3*H*-naphtho[2,1-*b*]pyrans) **36**, **37**, **38** and **43**.

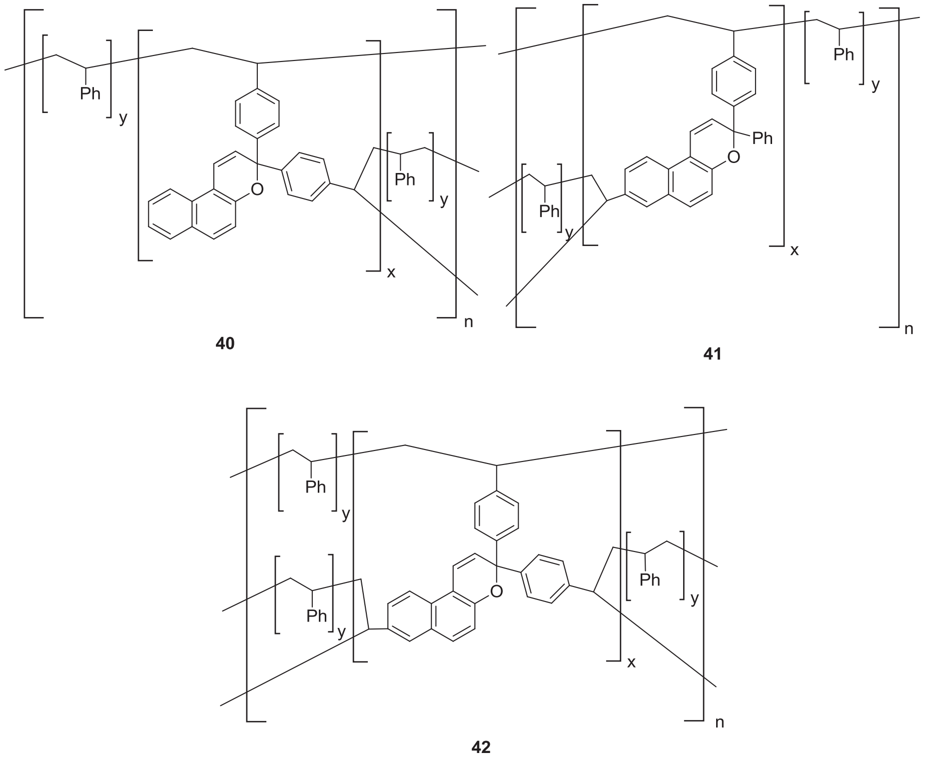
The 8-bromonaphthopyran **20** gave the longest wavelength absorbing photomerocyanine, with a maximum absorption at 448 nm. This maximum was shifted successively hypsochromically upon incorporation of further bromine atoms at the *p*-position of each of the C-3 phenyl rings, to afford **22** (446 nm) and **23** (440 nm), respectively (Fig. 3).

The vinyl substituted naphthopyrans gave bathochromically shifted absorption maxima relative to their bromine substituted precursors. The vinyl function serves as an electron releasing group and also as a means to extend conjugation. A C-3 *p*-vinyl substituted phenyl unit (**26**) shifts λ_{max} bathochromically by 10 nm relative to **25**, an effect which is somewhat additive since the incorporation of a second *p*-vinylphenyl unit to afford **30** results in a shift of λ_{max} to 458 nm. A similar trend in wavelength shifts to those noted, upon introduction of a *m*- and *o*-bromine atom was apparent for the introduction of a *m*- (**27**) and *o*-vinyl unit (**28**) (Fig. 4). In accord with the vinyl group behaving as an electron donating group, the tris-vinylnaphthopyran **32** affords the compound with the longest wavelength absorbing photomerocyanine (476 nm). The photomerocyanine resulting from the bis-vinyl compound **31** absorbs midway between **32** and **30**. This feature, when taken together with the data for the photochromic response of the bromonaphthopyrans, suggests that C-8 of the naphthalene unit is more sensitive to substituent variation than are the *o*-, *m*- and *p*-positions of a C-3 aryl unit [3].

The photomerocyanine that was derived from the irradiation of the biphenyl substituted naphthopyran **24** exhibits an absorption band at 446 nm as a consequence of the extended conjugation of the biphenyl unit. The introduction of a terminal vinyl group into **24**, to afford **33**, resulted in only a minor bathochromic shift in λ_{max} to 448 nm, with no discernible change in the persistence of the photomerocyanine.

3.4. *Photochromic properties naphthopyran–styrene copolymers*

The photochromic response of the naphthopyran–styrene copolymers **36**–**43** were examined in toluene solution and also as



Scheme 8. Representative structures of the polymers **40**–**42**.

a film that was deposited from dichloromethane on a microscope slide; λ_{max} and $t_{1/2}$ data are collated in Table 2.

Examination of the photochromic response of the polymers in toluene (Table 2) reveals that λ_{max} is shifted hypsochromically with respect to the vinyl monomers for the majority of the examples (Fig. 5) with the exception of the biphenyl system **43** and the *o*-vinylphenyl analogue **39**. The hypsochromic shift has been ascribed to the change in the nature of the vinyl group to an alkyl group upon addition polymerisation, with the resulting alkyl group (polymer backbone) behaving as a weak donor group by σ-conjugation, whereas the vinyl function may operate by π-orbital overlap extending overall conjugation. The variation in the persistence of the photogenerated colour, reported as $t_{1/2}$, is more noticeable for those examples in which an 8-vinyl unit has been involved namely **36**, **41** and **42**, and for which $t_{1/2}$ has increased. For **41** and **42**, it may be the case that polymerisation has occurred at each of the vinyl functions, leading to a degree of crosslinking that restricts the usually facile ring-closure to the colourless pyran during which the long axis of the molecule must undergo a significant reorganisation to permit the ring-closure. The fact that there is a less significant increase in the persistence of the colour for the photomerocyanine from **40**, derived from the 3,3-bis(4-vinylphenyl)naphthopyran **30**, where crosslinking may also be present, may be rationalised by the fact that the change in geometry upon ring-closure to the colourless pyran is far less significant.

In the biphenylvinyl-derived polymer **43** the change from vinyl to alkyl group has a negligible influence on the photochromic response as a consequence of the phenyl spacer.

The most significant influence of the polymerisation on the photochromic response was noted for the polymer **39** that was

Table 1
Photochromic response of bromo- and vinyl-naphthopyrans.

	λ_{max} nm	$t_{1/2}$ s
17	430	10
18	422	12
19	420	417
20	448	5
21	426	8
22	446	6
23	440	4
24	446	11
25	432	11
26	442	7
27	426	10
28	424	1162
29	454	10
30	458	8
31	468	11
32	476	9
33	448	11

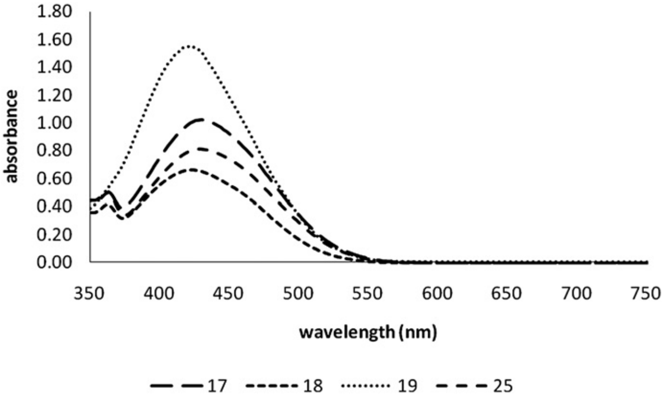


Fig. 2. Photochromic response of bromonaphthopyrans **17**–**19** and naphthopyran **25**.

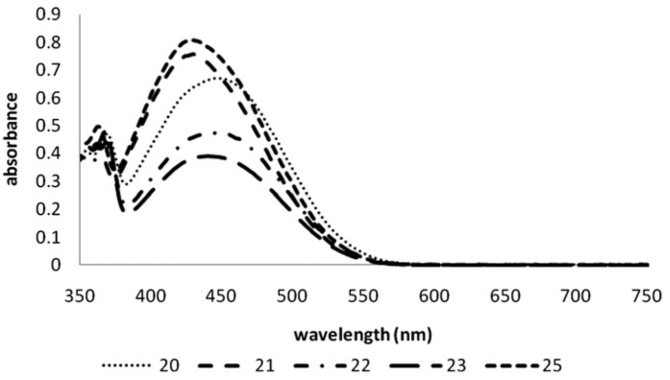


Fig. 3. Photochromic response of bromonaphthopyrans **21**–**23** and naphthopyran **25**.

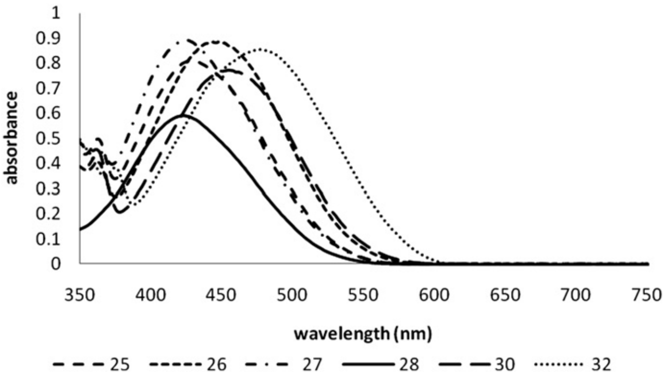


Fig. 4. Photochromic response of naphthopyran **25** and vinylnaphthopyrans **26**–**28**, **30** and **32**.

Table 2
Photochromic response of Poly(styrene-co-3*H*-naphtho[2,1-*b*]pyrans).

	λ_{max} nm (PhMe)	$t_{½}$ s (PhMe)	λ_{max} nm (film)
36	434	17	408
37	434	10	416
38	436	11	426
39	–	–	–
40	452	13	426
41	440	26	403
42	446	34	–
43	448	10	414

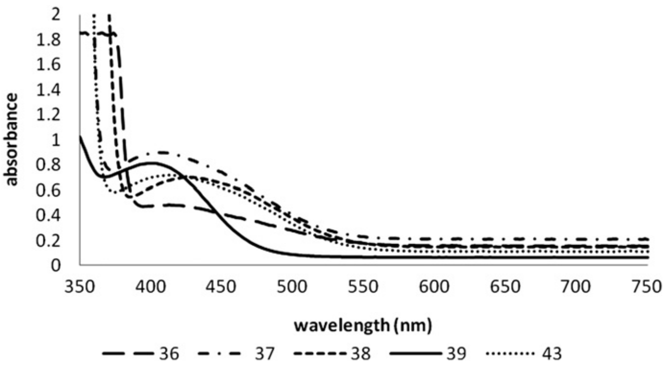


Fig. 5. Photochromic response of Poly(styrene-co-3*H*-naphtho[2,1-*b*]pyrans) **36**–**39** and **43**.

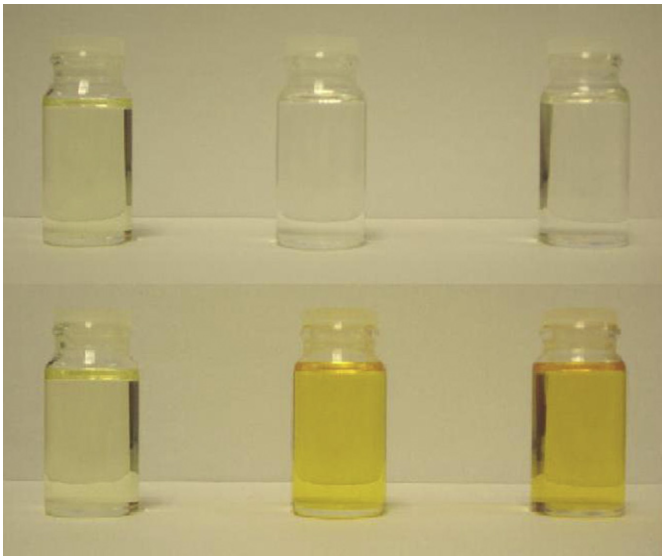
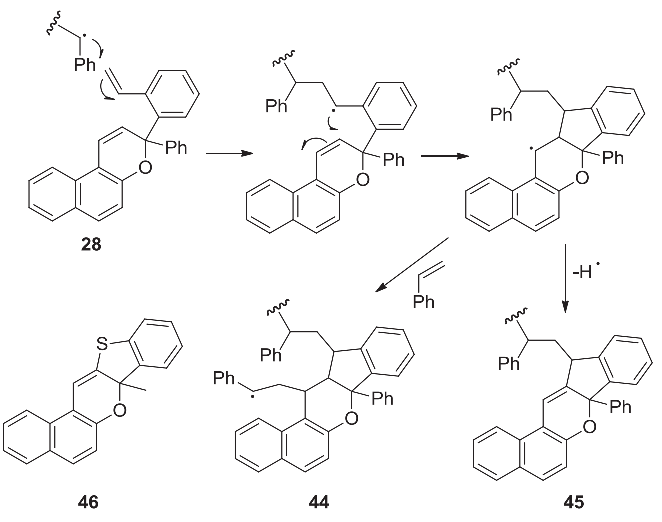


Fig. 6. Photochromic response of toluene solutions of Poly(styrene-co-3*H*-naphtho[2,1-*b*]pyrans) **39** (left), **38** (middle) and **37** (right) before (above) and after (below) irradiation.

derived from the 3-(2-vinylphenyl) substituted monomer **28** (Fig. 6). A yellow polymer resulted which displayed no photochromism. The reason for the absence of photochromism is not proven but we have speculated that, because of the close proximity of the vinyl group to the pyran ring double bond, a favourable 5-*exo-trig* cyclisation [30] is feasible, which may result in the destruction of the pyran ring double bond viz. **44** which cannot exhibit photochromism (Scheme 9). Alternatively, the cyclisation process may result in the pentacycle **45** though feasibly this could exhibit photochromism; a related photochromic compound **46** has been described by Irie though obtained by a different reaction process [31]. Further work is required to explore the postulated behaviour of **28** towards copolymerisation with styrene and to establish the true structure of the polymer **39**.

Table 2 also contains information concerning the λ_{max} of the polymers as thin films. The absence of toluene results in a further hypsochromic shift in λ_{max} for the majority of the samples the exception being polymer **42**. For polymer **42** photochromism was inhibited presumably by the extensive crosslinking that would



Scheme 9. Mechanistic rationale for the absence of photochromism of polymer **39**.

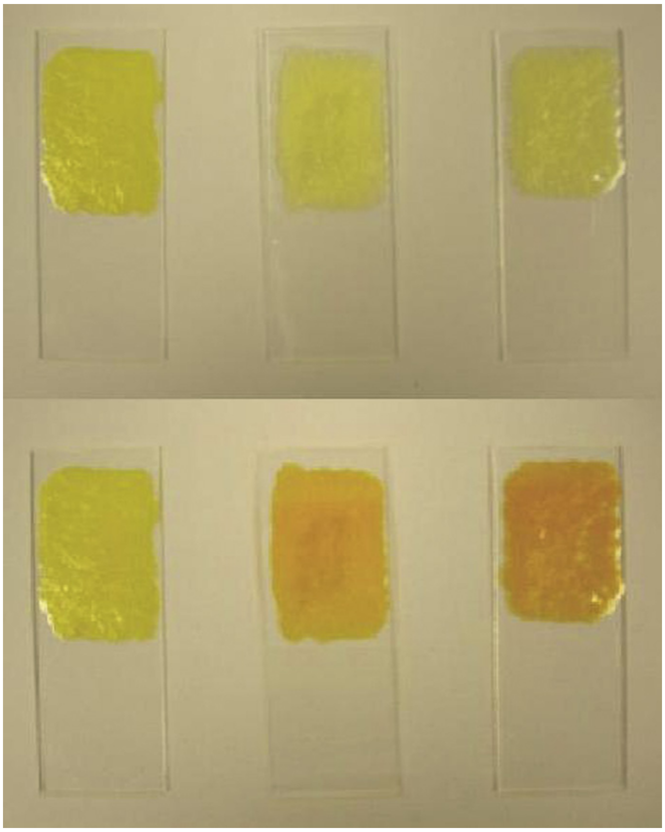


Fig. 7. Photochromic response of deposited films of Poly(styrene-co-3*H*-naphtho[2,1-*b*]pyrans) **39** (left), **38** (middle) and **37** (right) before (above) and after (below) irradiation.

severely restrict molecular motions. Toluene, which may serve either as a lubricant to facilitate ring-opening and ring-closing or to swell the crosslinked polymer, so as to enable the required molecular motions, is thus essential for photochromism to be observed. Fig. 7 displays images of the deposited films both before and after irradiation.

4. Conclusion

A comprehensive series of mono-, di- and tri-bromo-3*H*-naphtho[2,1-*b*]pyrans has been synthesised by the traditional union of a 2-naphthol with an alkynol. These bromonaphthopyrans are readily transformed, by a Suzuki coupling reaction with vinyl boronic anhydride pyridine complex, into their novel vinyl derivatives in generally good yield though the efficiency of the vinylation decreases with the increasing number of bromine atoms to be substituted. The vinylnaphthopyrans serve as complex analogues of styrene and readily undergo a thermally initiated free radical addition co-polymerisation with styrene to efficiently afford low molecular weight copolymers.

The photochromic response of the bromonaphthopyrans follows the established colour–structure relationships for photochromic naphthopyrans. The λ_{max} of the bromonaphthopyrans is shifted bathochromically upon replacement of the bromine atom with the vinyl group due to a combination of merocyanine chromophore extension and introduction of a better electron donor group. The photochromic response of toluene solutions of the copolymers was characterised by a hypsochromic shift of the λ_{max} that was induced by the change in hybridisation state of the C-atoms ($sp^2 \rightarrow sp^3$) of the vinyl function upon polymerisation. Increased half-lives were noted for the copolymers derived from the bis- and tris-vinylnaphthopyrans where some degree of crosslinking was expected and which hinders the ring-closing, colour fading reaction. A further hypsochromic shift in λ_{max} resulted for the thin films of the poly(styrene-co-naphthopyrans). Of particular note was the behaviour of the 3-(2-vinylphenyl)-3-phenylnaphthopyran which gave the typical yellow colour of the photomerocyanine coupled with the predictable large half-life. However, all photochromism of this naphthopyran was lost upon polymerisation suggesting that an alternative pathway supervenes in the expected polymerisation sequence.

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