JOURNAL OF Materials CHEMISTRY

Synthesis and properties of highly soluble third-order optically nonlinear chromophores and methacrylate monomer based on distyrylbenzene

M. S. Wong,[*a,b]† **M. Samoc,**[a] **A. Samoc,**[a] **B. Luther-Davies**[a] **and M. G. Humphrey**[b]

[a] *Australian Photonics Cooperative Research Centre, Laser Physics Centre, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT0200, Australia*

[b] *Department of Chemistry, The Australian National University, Canberra, ACT0200, Australia*

A novel series of highly soluble distyrylbenzenes bearing poly(alkyleneoxy) and/or alkylsulfonyl solubilizing substituents has been synthesized using the stereoselective Wadsworth–Emmons reaction as a key step. The corresponding poly(alkyleneoxy) alkylsulfonyl 4,4′-disubstituted distyrylbenzene has been covalently incorporated into an acrylic monomer which has also been successfully co-polymerized with methyl methacrylate (MMA). All the 4,4′-disubstituted distyrylbenzenes and the polyacrylate based co-polymer show excellent solubility, processibility and thermal stability. Importantly, 2-(2-butoxyethoxy)ethoxy-hexylsulfonyl 4,4′-disubstituted distyrylbenzene exhibits only a minor bathochromic shift of the absorption maximum compared to those of the corresponding symmetrically 4,4′-disubstituted distyrylbenzenes; however, its third-order optical nonlinearity derived from Z-scan measurements at 800 nm is approximately twice as large as those of its symmetrically 4,4′-disubstituted counterparts.

Poly(phenylenevinylene) (PPV) is one of the widely investigated π-conjugated polymeric materials exhibiting technologically useful multi-functional properties such as a large third-order optical nonlinearity,[1] an efficient electroluminescent response,[2] a high conductivity upon doping and a laser emission.[4] Unsubstituted PPV is insoluble in organic solvents and thin-films of this polymer are traditionally prepared by spin-casting of a water soluble polysulfonium precursor followed by pyrolysis.[5,6] However, the polydispersity and the poor structural perfection that are incurred in this preparation procedure may affect the optical and electrochemical properties of the polymeric thin-film. Over the last few years, various soluble PPV derivatives and copolymers have been synthesized to enhance the solubility and processibility as well as to tune the desirable properties.[7–9] With the solubilizing substituents influencing the electronic properties of the PPV chain, *e.g. via* induction and steric effects, and with the various compositions of the copolymers, the physical properties of the PPV-based materials are greatly varied. As a result, the exploration and development of efficient and useful PPV-based materials for a specific application still present a great challenge for the scientific communities.

It has recently been shown that highly π-conjugated PPV thin-films possess a large effective nonlinear refractive index and a desirable two-photon merit factor for all-optical switching.[10] This suggests that PPV-based materials may be potential candidates for applications in all-optical signal processing. It has also been shown that the third-order nonlinear optical properties of PPV originate from the relatively short π-conjugated chain segments of the polymer.[11] Therefore, it is of interest to understand and establish the structure–property relationship of the well-defined oligo-phenylenevinylenes (OPV) in order to further explore and optimize the PPV-based materials for photonic applications. Unfortunately, there are still no reliable guidelines for optimizing the second molecular hyperpolarizability, γ, of an organic molecule, in contrast to the first molecular hyperpolarizability, β. In addition, the (non)linear optical and thermal properties of PPV-based materials are greatly dependent upon the degree of π-conjugation, the co-planarity of the conjugated system and the electronic properties of the substituents. Towards the goal of understanding and establishing the structure–property relationship of OPVs, we report here our initial studies on the synthesis of a novel series of highly soluble three-phenyl-ring OPVs (distyrylbenzenes) bearing poly(alkyleneoxy) electron-donor(s) and/or hexylsulfonyl electron-acceptor(s). In addition, the influence of substitution on various physical properties including the absorption spectroscopic properties, the third-order nonlinear optical properties and the thermal behaviour will be discussed. For practical applications, the active chromophores or OPVs are required to be developed in the form of either side-chain or main-chain polymers in order to obtain better miscibility, a larger chromophore density and a higher thermal stability. Towards this end, we also report the synthesis of the acrylic monomer and polyacrylate bearing the corresponding donor–acceptor disubstituted distyrylbenzene unit.

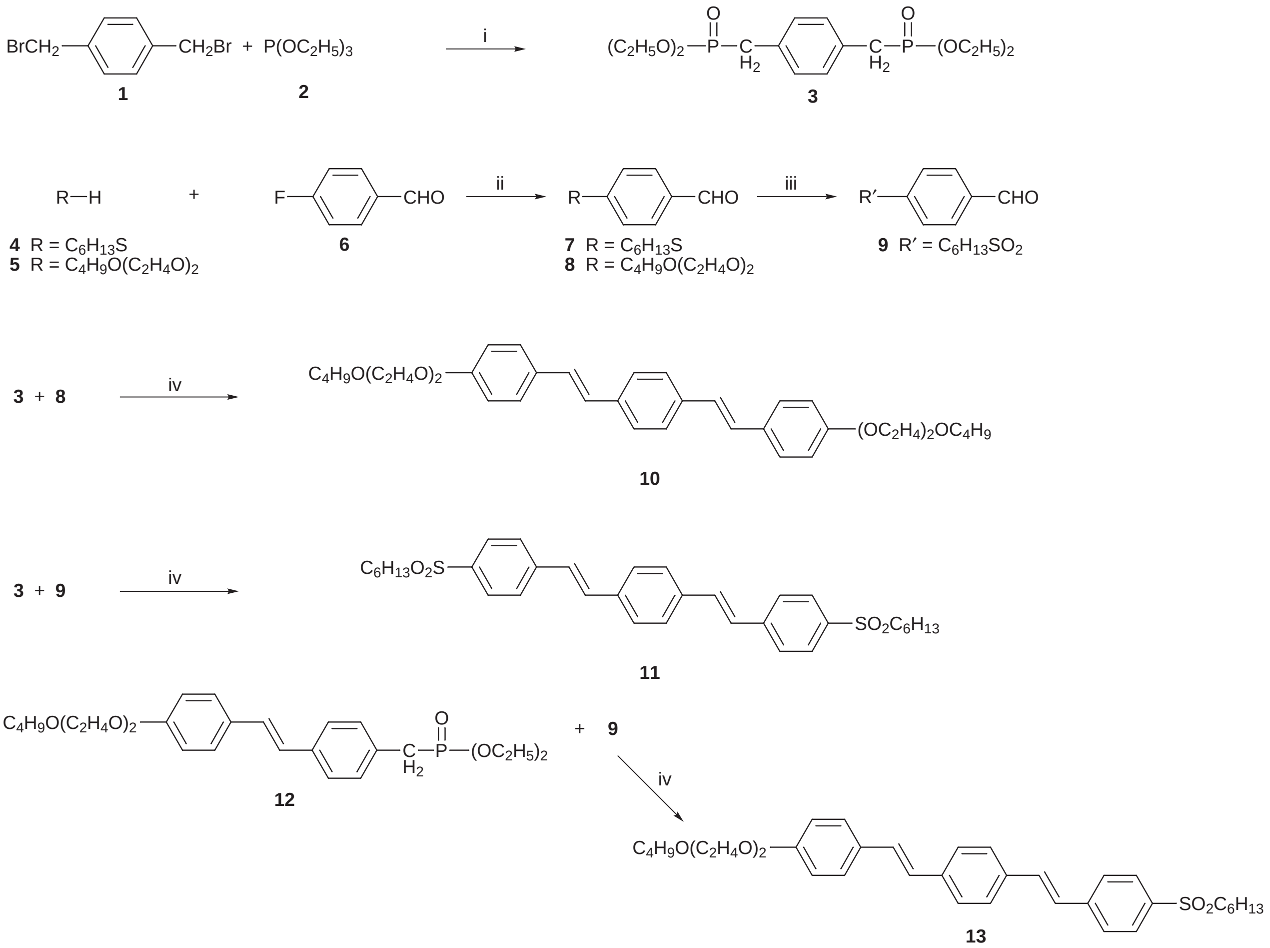
Results and Discussion

In general, any solubilizing substituent grafted on the lateral side of the main chain of an oligomer (including a vinylic linkage) will greatly distort the co-planarity of the π-conjugated system, leading to a decrease in conjugation and in desirable physical properties. Therefore, in this study, the solubilizing substituents will only be placed at the ends of the main chain of an oligomer. Although several symmetrically disubstituted distyrylbenzenes were previously synthesized for spectroscopic studies we have found that their solubilities were often too low to perform any reliable nonlinear optical measurement in solution [*e.g.* the solubility of 1,4-bis(-4-bromostyryl)benzene in chloroform is less than 0.1% w/w). To overcome this, the poly(alkyleneoxy) and alkylsulfonyl moieties were incorporated into the ends of the main chain to act as solubilizing as well as electron-donating and electron-withdrawing substituents, respectively.

The stereoselective Wadsworth–Emmons reaction was used to construct the *trans* carbon–carbon double bonds. The

---

† Present address: Department of Chemistry, Hong Kong Baptist University, Hong Kong.

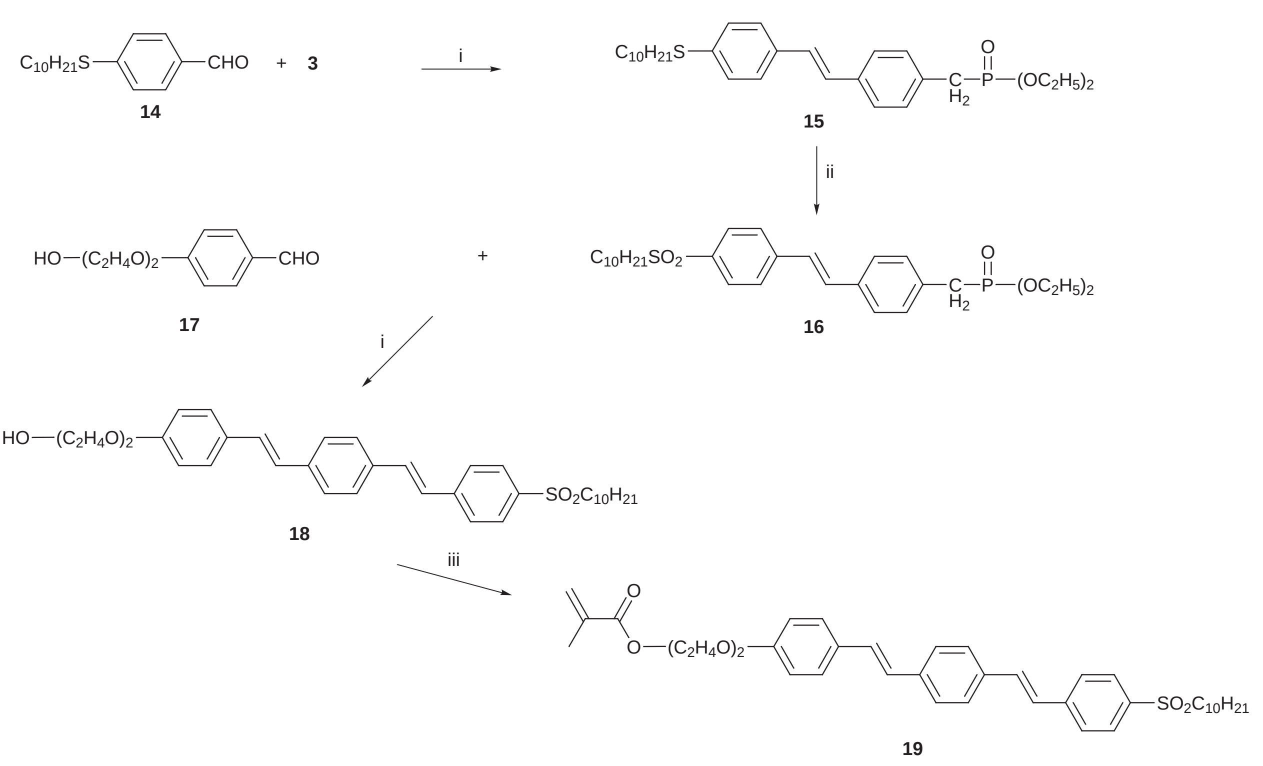


Scheme 1 *Reagents and conditions*: i, 150 °C; ii, K_2CO_3, DMSO, 150 °C; iii, MCPBA, CH_2Cl_2, 0 °C; iv, NaH, DME, room temp.

general scheme for the synthesis of symmetrically and unsymmetrically 4,4′-disubstituted distyrylbenzenes is summarized in Scheme 1. The bis-phosphonate **3** was prepared by the Michaelis–Arbuzov reaction using α,α′-dibromo-*p*-xylene **1** and triethyl phosphite **2**. The solubilizing hexylsulfanyl and 2-(2-butoxyethoxy)ethoxy substituents, were introduced by aromatic nucleophilic substitution of 4-fluorobenzaldehyde **6** affording the corresponding aldehydes **7** and **8**, respectively. The Wadsworth–Emmons reaction of the bis-phosphonate **3** with 2 equiv. of aldehyde **8** yielded the corresponding symmetrical distyrylbenzene **10**. Surprisingly, the yellow product obtained from the Wadsworth–Emmons reaction of **3** and 2 equiv. of **7** was not soluble enough to be characterized analytically by the conventional spectroscopic techniques. However, the oxidation of this yellow solid with 3-chloroperoxybenzoic acid (MCPBA) afforded the highly soluble distyrylbenzene **11**. Alternatively, the hexylsulfanyl functionality of **7** could be converted into the hexylsulfonyl functionality by means of MCPBA oxidation. Subsequent double Wadsworth–Emmons reactions also gave the desired distyrylbenzene **11**. To synthesize the donor–acceptor disubstituted distyrylbenzene **13**, the precursor mono-phosphonate **12** was first prepared from the reaction of the aldehyde **8** and excess of the bis-phosphonate **3**, followed by Wadsworth–Emmons reaction with aldehyde **9**. It was found that reversing the reaction sequence did not afford the desired product, as the corresponding mono-phosphonate could not be prepared directly from this method.

The synthetic route for the preparation of the methacrylate monomer bearing the poly(alkyleneoxy) alkylsulfonyl 4,4′-disubstituted distyrylbenzene is outlined in Scheme 2. A similar synthetic approach as used above was adopted to prepare the functionalized poly(alkyleneoxy) alkylsulfonyl 4,4′-disubstituted distyrylbenzene **18**. The reaction of the chromophore **18** with methacrylic anhydride in the presence of dimethylaminopyridine (DMAP) as catalyst and triethylamine as base afforded the methacrylate monomer **19**. To demonstrate the ability of this monomer to be polymerized, thermal radical polymerization conditions were employed to co-polymerize the methacrylate monomer **19** with MMA using the procedure described by Robello.[13] With an 8.3% w/w dye content in the feed composition, the estimated weight average of copolymer derived from gel permeation chromatography (GPC) is 35 000 g mol^{-1} with $T_g = 124$ °C. More detailed characterization and the physical properties of the copolymer will be reported elsewhere.

The results of the electronic absorption measurements, the third-order nonlinearities determined by Z-scan measurements using 800 nm irradiation wavelength and the thermal properties are summarized in Table 1. As seen from the electronic absorption spectra (Fig. 1), all the compounds show strong and intense low-lying absorption bands which indicate a highly π-conjugated system. Unlike the donor–acceptor 4,4′-disubstituted distyrylbenzene **13**, the low-lying absorption bands of the symmetrically 4,4′-disubstituted distyrylbenzenes **10** and **11** are apparently composed of several vibronic electronic transitions.[14] There are also significant bathochromic shifts of the absorption maxima λ_{max} of the 4,4′-disubstituted distyrylbenzenes compared to that of the unsubstituted distyrylbenzene ($\Delta\lambda = 12$–19 nm),[12] in spite of the moderate donating and withdrawing strength of the 2-(2-butoxyethoxy)ethoxy and hexylsulfonyl functionalities, respectively. Such a red shift is consistent with the fact that the donating and withdrawing substituents at the *para*-positions of distyrylbenzene enhance the π-electron delocalization along the entire unsaturated system. On the other hand, the donor–acceptor 4,4′-disubstituted distyrylbenzene **13** exhibits only a small bathochromic



Scheme 2 *Reagents and conditions*: i, NaH, DME, room temp.; ii, MCPBA, CH_2Cl_2; iii, DMAP, Et_3N, methacrylic anhydride, room temp.

Table 1 Summary of the measured physical properties of **10**, **11**, and **13**

Compound	λ_{max}/nm (ε/10^{-4} M^{-1} cm^{-1})	γ_{real}/ 10^{-36} esu	γ_{imag}/ 10^{-36} esu	transition temperature/ °C
10	368 (7.78)	200	54	46, 225
11	370 (7.62)	250	95	231, 259
13	375 (5.97)	420	200	216

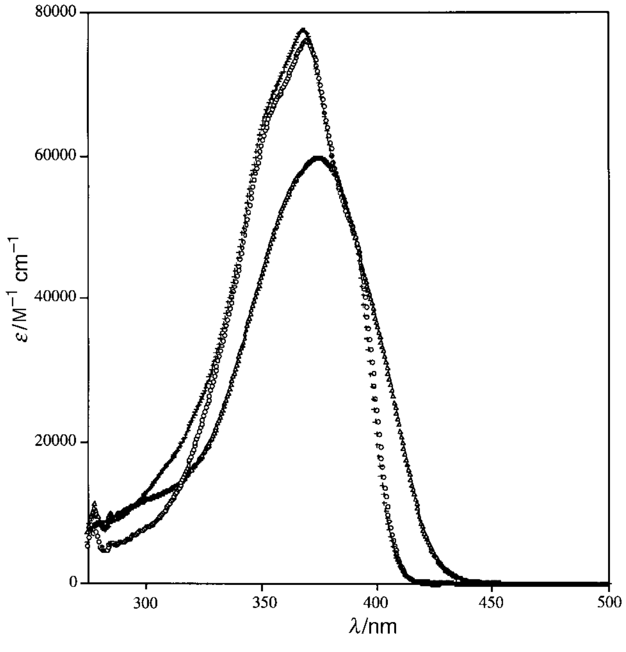


Fig. 1 Electronic absorption spectra of (+) **10**, (○) **11** and (△) **13** measured in chloroform

shift of λ_{max} compared to those of the symmetrically 4,4′-disubstituted analogues ($\Delta\lambda = 5$–7 nm). This is presumably due to the strong inductive nature of the hexylsulfonyl group.

To evaluate the third-order molecular nonlinearities, the Z-scan technique[15] was employed as it can determine the sign, the real part of the molecular nonlinearity γ_{real} (which relates to the refractive nonlinearity) and the imaginary part of the molecular nonlinearity γ_{imag} (due to the multi-photon absorption). All the 4,4′-disubstituted distyrylbenzenes exhibit positive γ_{real} values. In spite of the very different electronic nature of the 2-(2-butoxyethoxy)ethoxy and hexylsulfonyl functionalities, both of the symmetrically 4,4′-disubstituted distyrylbenzenes **10** and **11** show comparable γ_{real} values. On the other hand, the donor–acceptor 4,4′-disubstituted distyrylbenzene **13** exhibits an enhanced γ_{real} compared to those of its symmetrically disubstituted counterparts **10** and **11**. This confirms the advantage of using conjugated donor and acceptor substituents to enhance γ,[16] in particular the poly(alkyleneoxy) alkylsulfonyl pair which have been shown to provide an excellent transparency–nonlinearity trade-off. In contrast to their γ_{real} values, bis(hexylsulfonylstyryl)benzene **11** shows a substantially higher γ_{imag} than that of bis[2-(2-butoxyethoxy)ethoxystyryl]-benzene **10**. The γ_{imag} value of the donor–acceptor 4,4′-disubstituted distyrylbenzene **13** is also relatively large, presumably due to the relatively strong two-photon absorption at irradiation wavelength.

With the incorporation of the solubilizing substituents, the distyrylbenzene derivatives and the corresponding methacrylate monomer show enhanced solubility in various solvents; in particular, the donor–acceptor 4,4′-disubstituted distyrylbenzene **13** has a solubility of more than 6% w/w in chloroform. The solubilizing substituents also induce liquid crystalline phases of the symmetrically 4,4′-disubstituted distyrybenzenes (**10** and **11**).

Experimental

All the new compounds were fully characterized with standard spectroscopic techniques. All the physical measurements were performed in $CHCl_3$. ^{1}H NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are referenced to the residual $CHCl_3$ (7.24 ppm). Infrared spectra were recorded using a Perkin-Elmer System 2000 FT-IR spectrometer. Electronic absorption (UV–VIS) spectra were recorded using a Shimadzu UV-3101PC Spectrophotometer. Thermal properties were determined by differential scanning calorimetry (DSC) using a Shimadzu Thermal Analysis System TA-50ASI with a heating rate of 10 °C min^{-1}. The reported temperatures were the peak temperature of the traces obtained from the rerun. Molecular weight of the co-polymer was estimated by gel permeation chromatography (GPC) using a Spectra Physics HPLC instrument equipped with a Jordi Mixed-Bed GPC column. THF was used as the eluent with toluene as an internal standard. The polystyrene standards were used for the calibration.

Z-Scan measurements were performed with a system consisting of a Coherent Mira Ar-pumped Ti-sapphire laser generating a mode-locked train of approximately 100 fs 800 nm pulses and a Ti-sapphire regenerative amplifier pumped by a Q-switched pulsed YAG laser at 30 Hz. The open- and closed-aperture Z-scans were recorded at two or three concentrations for each compound, and the real and imaginary part of the nonlinear phase shift was determined by numerical fitting. The real and imaginary parts of the hyperpolarizability of the solute were calculated by assuming a linear concentration dependence of the solution susceptibility. The nonlinearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1} was assumed.

General procedure for the aromatic nucleophic substitution

To an equimolar solution of 4-fluorobenzaldehyde **6** (2 ml, 18.6 mmol) and the corresponding solubilizing substituent (*e.g.* **4**: 2.6 ml, 18.6 mmol) in DMSO was added 2 equiv. of Na_2CO_3 (*i.e.* 5.2 g, 37.3 mmol). The mixture was heated at 150 °C for 24 h under N_2. After cooling to room temp., the reaction mixture was poured into water and extracted twice with CH_2Cl_2, dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude product was then purified by silica gel chromatography using the gradient elution technique with CH_2Cl_2–ethyl acetate as eluent [affording 3.79 g (91%) of **7**].

4-Hexylsulfanylbenzaldehyde 7. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.73 (d, *J* 8.55 Hz, 2H), 7.31 (d, *J* 8.31 Hz, 2H), 2.97 (t, *J* 7.37 Hz, 2H), 1.68 (m, 2H), 1.29 (m, 2H), 1.28 (m, 4H), 0.86 (t, *J* 7.11 Hz, 3H).

4-[2-(2-Butoxyethoxy)ethoxy]benzaldehyde 8. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.79 (d, *J* 8.64 Hz, 2H), 6.99 (d, *J* 8.82 Hz, 2H), 4.19 (t, *J* 4.79 Hz, 2H), 3.86 (t, *J* 4.79 Hz, 2H), 3.70 (m, 2H), 3.58 (m, 2H), 3.43 (t, *J* 6.72 Hz, 2H), 1.53 (m, 2H), 1.32 (m, 2H), 0.87 (t, *J* 7.80 Hz, 3H).

4-Hexylsulfonylbenzaldehyde, 9

To a stirred solution of **7** (400 mg, 1.8 mmol) in CH_2Cl_2 at 0 °C was slowly added MCPBA (650 mg, 3.6 mmol). After stirring for 1 h, the white suspension was filtered off and the filtrate was washed with Na_2CO_3 solution, dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude product was then purified by silica gel chromatography using the gradient elution technique with CH_2Cl_2–ethyl acetate as eluent affording 350 g of **9** in 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.07 (s, 4H), 3.10 (t, *J* 8.09 Hz, 2H), 1.69 (m, 2H), 1.34 (m, 2H), 1.23 (m, 4H), 0.83 (t, *J* 6.78 Hz, 3H).

General procedure for the Wadsworth–Emmons reaction

To an equimolar solution of an aldehyde (*i.e.* **9**: 89 mg, 0.34 mmol) and the corresponding phosphonate ester (*i.e.* **12**: 170 mg, 0.34 mmol) in anhydrous DME was slowly added 1.2 equiv. of NaH (15 mg, 0.42 mmol) at 0 °C. After stirring for 0.5 h at 0 °C, the reaction mixture was slowly warmed up to room temp. After stirring for 2 h at room temp., the solution was quenched with water. The crude product was either collected by suction filtration or extracted twice with CH_2Cl_2, dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude product was then purified by silica gel chromatography using the gradient elution technique with CH_2Cl_2–ethyl acetate as eluent [affording 110 g (54%) of **13**]. For the double Wadsworth–Emmons reactions, a 2 : 1 mixture of aldehyde (*i.e.* **9**: 350 mg, 1.37 mmol) and phosphonate ester (*i.e.* **3**: 260 mg, 0.69 mmol) was used [affording 170 mg (43%) of **11**].

1,4-Bis{4-[2-(2-butoxyethoxy)ethoxy]styryl}benzene 10. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 4H), 7.42 (d, *J* 8.91 Hz, 4H), 7.05 (d, *J* 16.20 Hz, 2H), 6.94 (d, *J* 16.30 Hz, 2H), 6.89 (d, *J* 8.79 Hz, 4H), 4.15 (t, *J* 4.88 Hz, 4H), 3.86 (t, *J* 4.88 Hz, 4H), 3.71 (m, 4H), 3.60 (m, 4H), 3.46 (t, *J* 6.72 Hz, 4H), 1.55 (m, 4H), 1.35 (m, 4H), 0.90 (t, *J* 7.28 Hz, 6H). MS (EI) *m/z* 602.3 (M^+). HRMS (EI) $C_{38}H_{50}O_6$: calc. 602.3607 found, 602.3628. $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3029, 2934, 2875, 1605, 1516, 1457, 1250, 1176, 1111, 1065. Crystal–mesophase = 46 °C, mesophase–isotropic = 225 °C. Found: C, 75.60; H, 8.59. $C_{38}H_{50}O_6$ requires C, 75.72; H, 8.34%.

1,4-Bis[4-(hexylsulfonyl)styryl]benzene 11. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* 8.46 Hz, 4H), 7.66 (d, *J* 8.52 Hz, 4H), 7.55 (s, 4H), 7.25 (d, *J* 16.32 Hz, 2H), 7.15 (d, *J* 16.26 Hz, 2H), 3.08 (t, *J* 8.1 Hz, 4H), 1.70 (m, 4H), 1.34 (m, 4H), 1.24 (m, 8H), 0.84 (t, *J* 6.84 Hz, 6H). MS (EI) *m/z* 578.2 (M^+). HRMS (EI) $C_{34}H_{42}O_4S_2$: calc. 578.2525, found 578.2523. $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3018, 2930, 2859, 1592, 1511, 1466, 1310, 1142, 1089. Crystal–mesophase = 231 °C, mesophase–isotropic = 259 °C. Found: C, 70.47; H, 7.17; S, 10.94. $C_{34}H_{42}O_4S_2$ requires C, 70.55; H, 7.31; S, 11.08%.

Diethyl 4-{4-[2-(2-butoxyethoxy)ethoxy]styryl}benzylphosphonate 12. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* 8.79 Hz, 4H), 7.24 (dd, *J* 8.19 Hz, *J* 2.40 Hz, 2H), 7.01 (d, *J* 16.47 Hz, 2H), 6.89 (d, *J* 16.41 Hz, 1H), 6.88 (d, *J* 8.70 Hz, 2H), 4.12 (t, *J* 5.22 Hz, 2H), 3.99 (m, 4H), 3.84 (t, *J* 4.98 Hz, 2H), 3.70 (m, 2H), 3.58 (m, 4H), 3.58 (m, 2H), 3.44 (t, *J* 6.72 Hz, 2H), 3.12 (d, *J* 21.69 Hz, 1H), 1.55 (m, 2H), 1.32 (m, 2H), 1.22 (t, *J* 6.99 Hz, 6H), 0.89 (t, *J* 7.41 Hz, 3H).

1-{4-[2-(2-Butoxyethoxy)ethoxy]styryl}-4-(4-hexylsulfonylstyryl)benzene 13. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* 8.49 Hz, 2H), 7.64 (d, *J* 8.52 Hz, 2H), 7.49 (s, 4H), 7.43 (d, *J* 8.79 Hz, 2H), 7.23 (d, *J* 16.38 Hz, 1H), 7.10 (d, *J* 16.41 Hz, 1H), 7.09 (d, *J* 16.41 Hz, 1H), 6.95 (d, *J* 16.26 Hz, 1H), 6.90 (d, *J* 8.79 Hz, 2H), 4.14 (t, *J* 4.92 Hz, 2H), 3.86 (t, *J* 4.94 Hz, 2H), 3.71 (m, 2H), 3.59 (m, 2H), 3.46 (t, *J* 6.72 Hz, 2H), 3.07 (t, *J* 8.10 Hz, 2H), 1.70 (m, 2H), 1.56 (m, 2H), 1.33 (m, 4H), 1.24 (m, 4H), 0.90 (t, *J* 7.35 Hz, 3H), 0.84 (t, *J* 6.87 Hz, 3H). MS (EI) *m/z* 590.2 (M^+). HRMS (EI) $C_{36}H_{46}O_5S$: calc. 590.3066, found 590.3077. $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3029, 2960, 2933, 1591, 1514, 1459, 1307, 1250, 1176, 1143, 1111, 1089. Mp = 216 °C. Found: C, 73.20; H, 8.12; S, 5.16. $C_{36}H_{46}O_5S$ requires C, 73.19; H, 7.85; S, 5.43%.

Diethyl 4-(4-decylsulfanylstyryl)benzylphosphonate 15. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* 8.79 Hz, 2H), 7.40 (d, *J* 8.61 Hz, 2H), 7.27 (d, *J* 8.37 Hz, 2H), 7.02 (s, 2H), 4.00 (m, 4H), 3.14 (d, *J* 21.72 Hz, 2H), 2.91 (t, *J* 7.38 Hz, 2H), 1.62 (m, 2H), 1.40 (m, 2H), 1.23 (m, 20H), 0.86 (d, *J* 6.74 Hz, 3H). MS (EI) *m/z* 502.1 (M^+).

Diethyl 4-(4-decylsulfonylstyryl)benzylphosphonate 16. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* 8.46 Hz, 2H), 7.63 (d, *J*

8.55 Hz, 2H), 7.47 (d, *J* 7.92 Hz, 2H), 7.30 (dd, *J* 8.31 Hz, *J* 2.46 Hz, 2H), 7.21 (d, *J* 16.47 Hz, 1H), 7.08 (d, *J* 16.26 Hz, 1H), 4.01 (m, 4H), 3.14 (d, *J* 21.96 Hz, 2H), 3.06 (t, *J* 8.01 Hz, 2H), 1.69 (m, 2H), 1.23 (m, 22H), 0.86 (d, *J* 6.75 Hz, 3H). MS (EI) *m/z* 534.1 (M^+).

1-{4-[2-(2-Hydroxyethoxy)ethoxy]styryl}-4-(4-decylsulfonylstyryl)benzene 18. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* 8.46 Hz, 2H), 7.65 (d, *J* 8.46 Hz, 2H), 7.50 (s, 4H), 7.45 (d, *J* 8.64 Hz, 2H), 7.23 (d, *J* 16.24 Hz, 1H), 7.11 (d, *J* 16.20 Hz, 1H), 7.09 (d, *J* 16.26 Hz, 1H), 6.96 (d, *J* 16.41 Hz, 1H), 6.91 (d, *J* 8.82 Hz, 2H), 4.15 (s, 2H), 3.87 (s, 2H), 3.76 (m, 2H), 3.67 (m, 2H), 3.07 (t, *J* 7.80 Hz, 2H), 1.70 (m, 2H), 1.21 (m, 16H), 0.85 (t, *J* 6.69 Hz, 3H). MS (FAB) *m/z* 590.1 (M^+).

Synthesis of 19

To a stirred solution of **18** (240 mg, 0.41 mmol), freshly distilled methacrylic anhydride (75 mg, 0.49 mmol) and 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (15 mg, 0.04 mmol) in anhydrous CH_2Cl_2 at room temp. was slowly added a solution of DMAP (6 mg, 0.04 mmol) and Et_3N (49 mg, 0.49 mmol) in CH_2Cl_2. The reaction was monitored by TLC. After complete disappearance of **18** *via* TLC, the reaction mixture was quenched with water and extracted twice with CH_2Cl_2, dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude product was purified by silica gel chromatography using the gradient elution technique with CH_2Cl_2–ethyl acetate as eluent, affording 125 mg (47%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* 8.46 Hz, 2H), 7.65 (d, *J* 8.55 Hz, 2H), 7.50 (s, 4H), 7.44 (d, *J* 8.79 Hz, 2H), 7.23 (d, *J* 16.38, 1H), 7.11 (d, *J* 16.47, 1H), 7.09 (d, *J* 16.41, 1H), 6.96 (d, *J* 16.35 Hz, 1H), 6.90 (d, *J* 8.82 Hz, 2H), 6.12 (m, 1H), 5.56 (m, 1H), 4.33 (t, *J* 4.80 Hz, 2H), 4.14 (t, *J* 4.59 Hz, 2H), 3.87 (t, *J* 4.77 Hz, 2H), 3.82 (t, *J* 4.86 Hz, 2H), 3.07 (t, *J* 7.95 Hz, 2H), 1.93 (m, 3H), 1.70 (m, 2H), 1.21 (m, 16H), 0.85 (t, *J* 6.42 Hz, 3H). MS (EI) *m/z* 658.3 (M^+). HRMS (EI) $C_{60}H_{50}O_6S$: calc. 658.3328, found 658.3336. $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3029, 2929, 2857, 1718, 1591, 1514, 1299, 1250, 1176, 1141, 1089. Mp = 213 °C; decomp. temp. = 290 °C.

Conclusions

A novel series of poly(alkyleneoxy) and/or alkylsulfonyl 4,4′-disubstituted distyrylbenzenes has been synthesized. Furthermore, the distyrylbenzene-derived methacrylate monomer has been synthesized by adopting the synthetic route developed. The thermal free-radical copolymerization of distyrylbenzene-derived methacrylate monomer with MMA has been shown to be achievable. All distyrylbenzene derivatives show excellent solubility, processibility and thermal stability. In addition to enhanced third-order nonlinearity, the 2-(2-butoxyethoxy)ethoxyhexylsulfonyl 4,4′-disubstituted distyrylbenzene exhibits an excellent transparency–nonlinearity trade-off compared to those of the symmetrically 4,4′-disubstituted distyrylbenzenes.

We gratefully acknowledge the Australian Photonics Cooperative Research Centre for financial support and N. T. Lucas for the GPC analysis. M.G.H. is an ARC Australian Research Fellow.

References

1. B. Luther-Davies and M. Samoc, *Curr. Opin. Solid State Phys.*, 1997, **2**, 213.
2. J. Burroughs, D. D.Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
3. M. Hirooka, I. Murase, T. Ohnishi and T. Noguchi, in *Frontiers of Macromolecular Science*, ed. T. Saegusa, Blackwell Scientific Publications, Oxford, UK, 1989, p. 425.
4. F. Hide, M. A. Diaz-Garcia, B. J. Schwartz and A. I. Heeger, *Acc. Chem. Res.*, 1997, **30**, 430.
5. D. R. Gagnon, J. D. Capistran, F. E. Karasz and R. W. Lenz, *Polym. Bull.*, 1984, **12**, 293.
6. S. Antoun, F. E. Karasz and R. W. Lenz, *J. Polym. Sci.*, *Part A*, 1988, **26**, 1809.
7. Z. Bao, Y. Chen, R. Cai and L. Yu, *Macromolecules*, 1993, **26**, 5281.
8. R. M. Gurge, A. Sarker, P. M. Lahti, B. Hu and F. E. Karasz, *Macromolecules*, 1996, **29**, 4287.
9. T. Maddux, W. Li and L. Yu, *J. Am. Chem. Soc.*, 1997, **119**, 844.
10. A. Samoc, M. Samoc, M. Woodruff and B. Luther-Davies, *Opt. Lett.*, 1995, **20**, 1241.
11. C. Bubeck, in *Organic Thin Films for Waveguiding Nonlinear Optics*, ed. F. Kajzar and J. D. Swalen, Gordon and Breach Publishers, Amsterdam, The Netherlands, 1996, p. 137.
12. S. Nakatsuji, K. Matsuda, Y. Uesugi, K. Nakashima, S. Akiyama, G. Katzer and W. Fabian, *J. Chem. Soc.*, *Perkin Trans. 2*, 1991, 861.
13. D. R. Robello, *J. Polym. Sci.*, *Part A: Polym. Chem.*, 1990, **28**, 1.
14. N. N. Barashkov, D. J. Guerrero, H. J. Olivos and J. P. Ferrais, *Synth. Met.*, 1995, **75**, 153.
15. M. Samoc, A. Samoc, B. Luther-Davies, Z. Bao, L. Yu, B. Hsieh and U. Scherf, *J. Opt. Soc. Am. B*, 1998, **15**, 817.
16. C. Bosshard, R. Spreiter, P. Günter, R. R. Tykwinski, M. Schreiber and F. Diederich, *Adv. Mater.*, 1996, **8**, 231.

Paper 8/03229G; *Received* 29*th April*, 1998