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Synthesis and bulk polymerisation of T-shaped enynes

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Novel T-shaped enynes have been synthesised and polymerised in the bulk to produce conjugated polymers with third order non-linear susceptibility as high as 10^{-9} e.s.u.

Progress in non-linear optical (NLO) materials in the past decade has been stimulated by the development of organic materials.[1]

The present authors are currently developing new types of NLO materials; among them polymers with discrete conjugated units which combine good environmental stability, solubility and film-forming properties with reasonably high $\chi^{(3)}$ values.[2–6] Another type of NLO material are polymers, obtained by the molten-state polymerisation of aromatic diacetylenes. When polymerised in the molten state some aromatic diacetylenes produce polymers as a transparent red glass.[7] They showed $\chi^{(3)}$ values up to 10^{-10} e.s.u.

This paper deals with the synthesis and bulk polymerisation of T-shaped derivatives of , -diethynylphenyl styrene bearing donor allyloxy and acceptor nitro groups.† As has been shown earlier, the diacetylenes bearing a , -diethynylphenyl styrene group have low melting points and polymerise rapidly in the molten state to produce a transparent glassy polymer with $\chi^{(3)}$ of 10^{-10} e.s.u.[7]

The key step in the synthesis of low molecular weight precursors in the Heck reaction between , -dibromostyrene derivatives **3** and **11** prepared from the corresponding benzaldehydes **2** and **10** by the Wittig reaction, and previously synthesised substituted phenyl acetylenes **5** and **9**. The Heck reaction between compounds **10** and **9** gave monosubstituted enyne **13** in addition to the main product **12**. Compound **13** is also highly unsaturated, bears donor and acceptor groups, and was polymerised in the bulk. Most likely, the formation of a considerable amount of compound **13** in contrast to the Heck reaction between compounds **2** and **5** where no monosubstituted side product was isolated is connected with the low acidity of acetylene **9** compared to **5**, making the Heck reaction more difficult. The structure of the monomers **6**, **12** and **13** was

Table 1 Some properties of low molecular weight precursors and the respective polymers.

Compound	mp/ °C	$\lambda^{a}_{\max}$/ nm	$\tau^{b}_{\rm polym}$/ min	$T^{c}_{\rm polym}$/ °C	T^{d}_{10}/ °C	$T^{e}_{\max}$/ °C	$\chi^{(3)}\times10^{-10}$ (e.s.u.)
6	192	372	3	200	310	250	30
12	107	387	5	170	280	175	16
13	200	365	2	210	240	250	—

[a]Long-wave absorption maximum. [b]Polymerisation time. [c]Polymerisation temperature. [d]10% weight loss temperature (heating rate 10 °C min^{-1}). [e]Exotherm maximum.

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† *Experimental.* 4-Ethynylnitrobenzene **5**, 4-allyloxybenzaldehyde **2** and 4-allyloxyiodobenzene **8** were prepared according to the literature.[8–10] Methylene dichloride was distilled over CaH_2. Other reagents were used as received from Aldrich. The synthesis of the monomers is shown in Scheme 1.

Solution ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, in $CDCl_3$ with TMS as an internal standard. Solid-state NMR spectra were recorded on a CMX-300 spectrometer at 75.5 MHz. Thermal polymerisation of monomers was carried out as follows: 0.01 g of the monomer was sandwiched between glass-plates and heated under nitrogen. The temperatures and polymerisation times are listed in Table 1. The solid dark-red glassy polymer formed between glass plates was used to measure $\chi^{(3)}$ values.

4-*Allyloxybenzaldehyde* **2**: ^{1}H NMR, δ: 9.87 (s, 1H, CHO), 7.82 (d, 2H, arom., *ortho* to CHO, *J* 8.7 Hz), 7.00 (d, 2H, arom., *meta* to CHO, *J* 8.7 Hz), 6.11–5.98 (m, 1H, $OCH_2CH{=}CH_2$), 5.44–5.30 (m, 2H, $OCH_2CH{=}CH_2$), 4.62 (td, 2H, $OCH_2CH{=}CH_2$, *J* 1.5 Hz, *J* 5.4 Hz); ^{13}C NMR, δ: 170.3 (CHO), 163.8 (C_{ar}–O–), 132.5 (–CH=), 131.9 (C_{ar} *ortho* to CHO), 130.0 (C_{ar}–CHO), 118.5 (CH_2=) 115.0 (C_{ar} *meta* to CHO), 69.0 (CH_2).

4-*Allyloxy-* , *-dibromostyrene* **3**: ^{1}H NMR, δ: 7.47 (d, 2H, *ortho* to $CH{=}CBr_2$, *J* 8.7 Hz), 7.37 (s, 1H, $-CH{=}CBr_2$), 6.87 (d, 2H, *meta* to $CH{=}CBr_2$, *J* 8.7 Hz), 6.08–5.96 (m, 1H, –CH=), 5.40–5.25 (m, 2H, $=CH_2$), 4.52 (d, $-OCH_2$, *J* 5.4 Hz); ^{13}C NMR, δ: 158.7 (C_{ar}–O–), 136.3 ($-CH{=}CBr_2$), 132.9 (–CH=), 129.8 (C_{ar} *meta* to –O–), 127.9 (C_{ar}–$CH{=}CBr_2$), 117.8 ($=CH_2$), 114.6 (C_{ar} *ortho* to –O–), 87.3 ($=CBr_2$), 68.7 (CH_2).

4-*Ethynylnitrobenzene* **5**: mp 152–153 °C. ^{1}H NMR, δ: 8.20 (d, 2H, *ortho* to NO_2, *J* 8.7 Hz), 7.62 (d, 2H, *meta* to NO_2, *J* 8.7 Hz), 3.35 (s, 1H, HC≡C–).

4-*Allyloxy-* , *-di(ethynyl-4′-nitrophenyl)styrene* **6**: mp 192–193 °C, yield 32%. ^{1}H NMR, δ: 8.28–8.21 (m, 4H, H^{14}, $H^{14'}$), 7.90 (d, 2H, H^5, *J* 8.7 Hz), 7.68–7.60 (m, 4H, H^{13}, $H^{13'}$), 7.27 (s, 1H, H^8), 6.98 (d, 2H, H^5, *J* 8.7 Hz), 6.14–6.01 (m, 1H, H^2), 5.48–5.31 (m, 2H, H^1), 4.61 (td, 2H, *J* 1.5 Hz, *J* 5.1 Hz); ^{13}C NMR, δ: 160.3 (C^4), 147.13 and 147.12 (C^{15} and $C^{15'}$), 146.3 (C^8), 133.4 (C^2), 132.3 and 131.2 (C^{14}, $C^{14'}$ and C^6), 129.9 and 129.8 (C^{12} and $C^{12'}$), 128.1 (C^7), 123.8 and 123.7 (C^{13} and $C^{13'}$), 118.1 (C^1), 114.9 (C^5), 99.0, 98.9, 94.0, 92.2 and 91.6 (C^9, C^{10}, $C^{10'}$, C^{11} and $C^{11'}$), 68.9 (C^3).

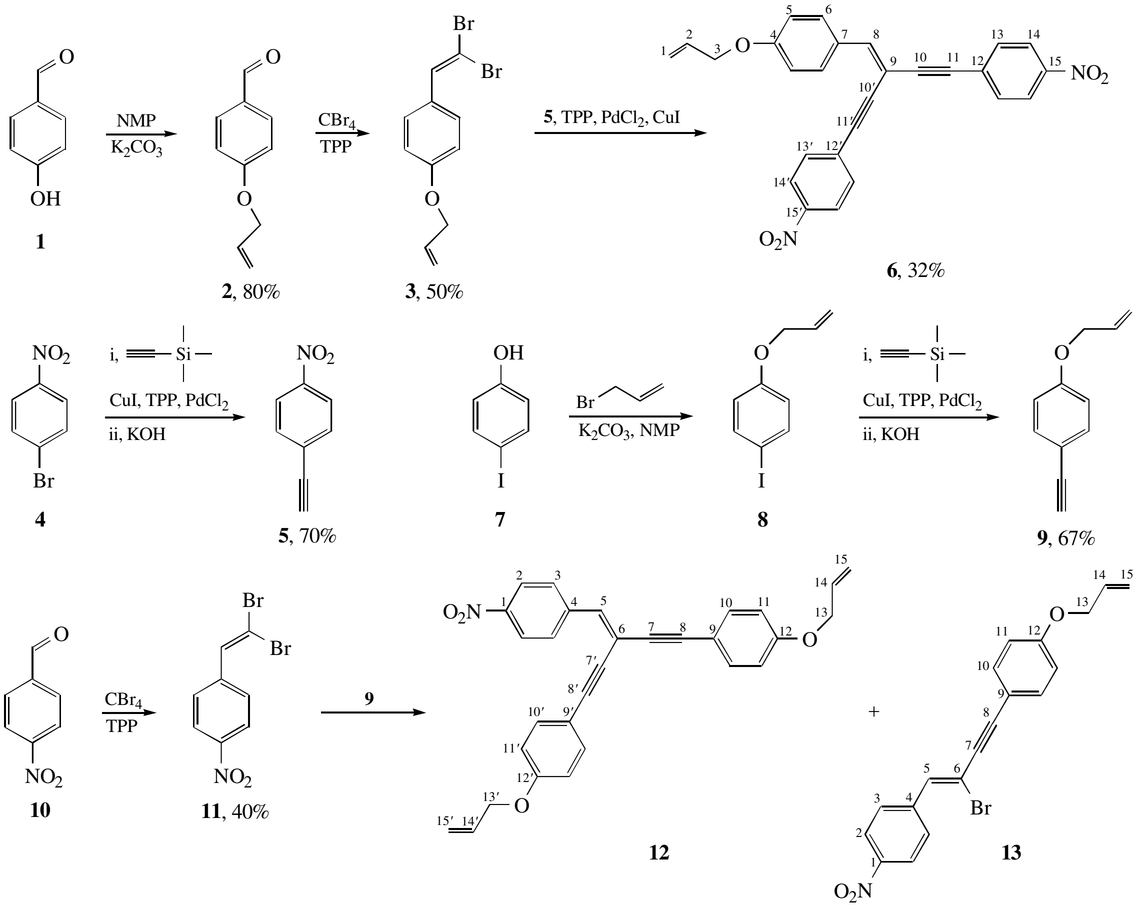
4-*Allyloxyiodobenzene* **8**: ^{1}H NMR, δ: 7.52 (d, 2H, *ortho* to I, *J* 9.0 Hz), 6.67 (d, 2H, *meta* to I, *J* 9.0 Hz), 6.07–5.94 (m, 1H, =CH–), 5.41–5.25 (m, 2H, $=CH_2$), 4.48 (td, 2H, *J* 1.5 Hz, *J* 5.1 Hz).

4-*Ethynylallyloxybenzene* **9**: overall yield 67%. ^{1}H NMR, δ: 7.40 (d, 2H, *meta* to –O–, *J* 8.7 Hz), 6.83 (d, 2H, *ortho* to –O–, *J* 8.7 Hz), 6.08–5.96 (m, 1H, =CH–), 5.42–5.25 (m, 2H, $=CH_2$), 4.80 (td, 2H, $-CH_2-$, *J* 1.5 Hz, *J* 5.1 Hz), 2.98 (s, 1H, ≡CH); ^{13}C NMR, δ: 159.0 (C_{ar}–O), 133.6 (C_{ar} *meta* to –O–), 132.9 (=CH–), 117.9 ($=CH_2$), 114.8 (C_{ar} *ortho* to –O–), 114.4 (C_{ar}–C≡), 83.7 (–C≡), 75.81 (≡CH), 68.8 (CH_2).

4-*Nitro-* , *-dibromostyrene* **11**: mp 48–50 °C. ^{1}H NMR, δ: 8.20 (d, 2H, *ortho* to NO_2, *J* 7.2 Hz), 7.68 (d, 2H, *meta* to NO_2, *J* 7.2 Hz), 7.56 (s, 1H, $CH{=}CBr_2$); ^{13}C NMR, δ: 147.3 (C_{ar}–NO_2), 141.5 (C_{ar}–$CH{=}CBr_2$), 135.0 ($-CH{=}CBr_2$), 129.2 (C_{ar} *ortho* to NO_2), 123.8 (C_{ar} *meta* to NO_2), 94.1 ($=CBr_2$).

4-*Nitro-* , *-di(ethynyl-4′-allyloxyphenyl)styrene* **12** and 4-*nitro-* *-bromo-* *-(ethynyl-4′-allyloxyphenyl)styrene* **13**: a solution of compound **11** (2.9 g, 4.4 mmol), compound **9** (3.0 g, 2.94 mmol), TPP (0.7 g), CuI (0.02 g) and $PdCl_2\cdot(TPP)_2$ (0.004 g) in triethylamine (60 ml) was refluxed under nitrogen for 6 h. The solvent was evaporated *in vacuo* and the residue was rinsed with water and chromatographed on SiO_2 with CCl_4 giving compounds **12** and **13** with yields of 31% and 25%, respectively. Compound **12**: mp 106–107 °C. ^{1}H NMR, δ: 8.22 (d, 2H, H^2, *J* 8.7 Hz), 6.90 (d, 2H, H^3, *J* 8.7 Hz), 7.47 (d, 4H, H^{10} and $H^{10'}$, *J* 8.7 Hz), 7.10 (s, 1H, H^5), 6.94–6.87 (m, 4H, H^{11} and $H^{11'}$), 6.12–5.99 (m, 2H, H^{14} and $H^{14'}$), 5.45–5.29 (m, 4H, H^{15} and $H^{15'}$), 4.59–4.55 (m, 4H, H^{13} and $H^{13'}$); ^{13}C NMR, δ: 159.6 and 159.3 (C^{12} and $C^{12'}$), 147.1 (C^1), 142.2 (C^4), 138.3 (C^5), 133.4 (C^{10} and $C^{10'}$), 133.1 and 132.9 (C^{14} and $C^{14'}$), 129.2 and 123.7 (C^2 and C^3), 118.1 and 118.0 (C^{15} and $C^{15'}$), 115.2 and 115.0 (C^{11} and $C^{11'}$), 114.7 and 114.4 (C^9 and $C^{9'}$), 108.5 (C^6), 96.8, 90.7, 87.9 and 85.7 (C^7, C^8, $C^{7'}$ and $C^{8'}$), 68.9 (C^{13} and $C^{13'}$).

Compound **13**: mp 199–200 °C. ^{1}H NMR, δ: 8.20 (d, 2H, H^2, *J* 9.0 Hz), 7.63 (d, 2H, H^3, *J* 9.0 Hz), 7.47 (d, 2H, H^{10}, *J* 9.0 Hz), 7.26 (s, 1H, H^5), 6.88 (d, 2H, H^{11}, *J* 9.0 Hz), 6.10–5.97 (m, 1H, H^{14}), 5.44–5.29 (m, 2H, H^{15}), 4.65 (td, 2H, *J* 1.5 Hz, *J* 5.1 Hz); ^{13}C NMR, δ: 159.9 (C^{12}), 147.4 (C^1), 134.3 and 133.1 (C^2, C^{10} and C^5), 132.6 (C^{14}), 123.7 (C^3), 118.1 (C^{15}), 115.1 (C^{11}), 113.2 (C^9), 84.8, 79.5 and 78.7 (C^6, C^7 and C^8), 68.9 (C^{13}).



TPP: triphenylphosphine NMP: *N*-methylpyrrolidone

Scheme 1 Monomer synthesis.

confirmed by standard spectroscopic techniques FT-IR and ^{1}H and ^{13}C NMR.

According to DSC data the polymerisation exotherms appeared immediately after the melting transition. The decomposition temperatures of the monomers **6** and **12** are of 310 and 280 °C, respectively, while compound **13** starts to decompose at 240 °C (Table 1). The low thermal stability and high melting point of **13** are due to the weak C–Br bond and the rigid linear structure of the molecule, respectively. In addition to the widest temperature range between melting point and decomposition temperature compound **12** has the most polarizable -electron system as followed by long-wave absorption maxima (Table 1).

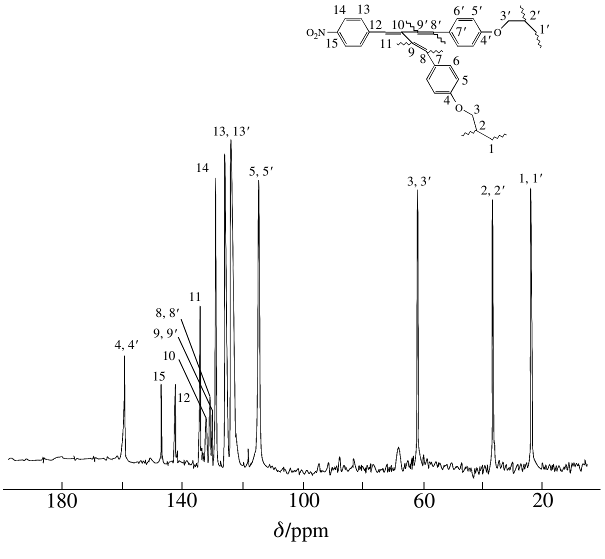
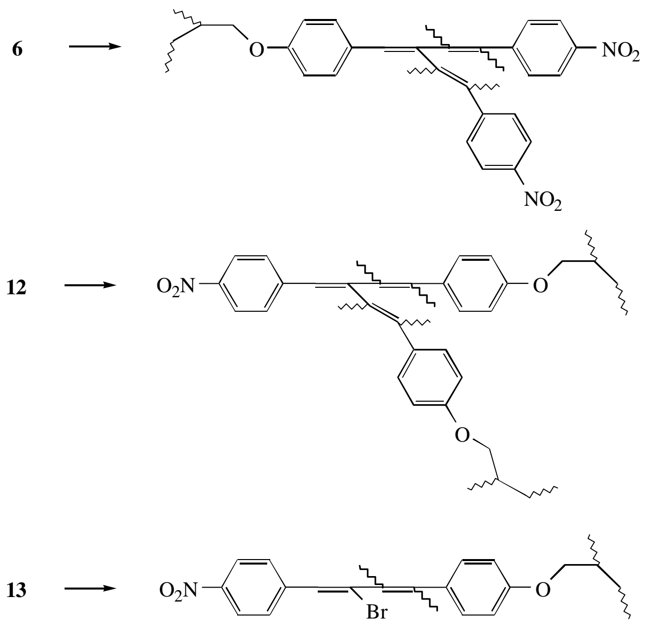


Figure 1 Solid-state NMR spectra of poly-**12** (^{1}H 90° pulse width 5 s, cross-polarisation contact time 2 ms, spinning frequency 4 kHz).

All monomers polymerised in the bulk above the melting point at temperatures listed in Table 1 to produce insoluble and transparent red polymers. In the case of compound **13** the polymer obtained was not completely transparent, probably due to partial thermal composition during the polymerisation as a result of which its $\chi^{(3)}$ values could not be measured. Indeed, in the FT-IR spectra of poly-**13** a significant decrease in C–Br stretching intensity at 685 cm^{-1} compared to **13** is observed. According to solid-state ^{13}C NMR spectra polymerisation in the bulk produced polymers with a rather defined structure consisting of substituted polyacetylene sequences interconnected by polyolefin cross-links. Figure 1 shows the assigned solid-state ^{13}C NMR spectrum of poly-**12** as an example. Confirming the NMR data the FT-IR analysis shows that a very intense C≡C stretching at 2210 cm^{-1} in the monomers almost disappeared in the polymers. A weak peak at 1645 cm^{-1} due to the allylic C=C of **12** is missing from the spectra of poly-**12**. However, out-of-plane =CH deformation vibrations are still seen at 985 cm^{-1}. Other functional groups such as nitro (1518 and 1338 cm^{-1}) and ether (1250 and 1150 cm^{-1}) were unaffected by the polymerisation. On this basis the polymerisation route is shown in Scheme 2.

$\chi^{(3)}$ data for poly-**6** and poly-**12** obtained by using a picosecond laser consisting of a mode locked Quantel Nd:YAG laser with frequency doubled to 532 nm are listed in Table 1. It was difficult to obtain reliable data for poly-**13** due to the poor optical quality of the polymer glass forming on polymerisation **13** as mentioned before. As seen, poly-**6** and poly-**12** show high $\chi^{(3)}$ values, > 10^{-9} e.s.u. This is one order of magnitude higher than that of the similar molten-state polymerised compound bearing a , -diethynylphenylstyrene group.[17] In all likelihood it is the polyacetylene sequences substituted by donors and acceptors that contributes to the high $\chi^{(3)}$ values of poly-**6** and poly-**12**.[2]



Scheme 2 Bulk polymerisation.

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