Synthesis and bulk polymerisation of T-shaped enynes

Sergei M. Fomine,*[a] Lyudmila Yu. Fomina,[a] Rocío Jiménez,[a] Elena Popova[b] and Takeshi Ogawa Murata[a]

[a] *Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán, México DF 04510, México. Fax: +5 25 616 1201; e-mail: fomine@servidor.unam.mx*
[b] *L. Ya. Karpov Institute of Physical Chemistry, 103064 Moscow, Russian Federation. Fax: +7 095 975 2450*

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 β,β-diethynylphenyl styrene bearing donor allyloxy and acceptor nitro groups.† As has been shown earlier, the diacetylenes bearing a β,β-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 β,β-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	λ^{a}_{max}/ nm	τ^{b}_{polym}/ min	T^{c}_{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.

† *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*-β,β-*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*-β,β-*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).

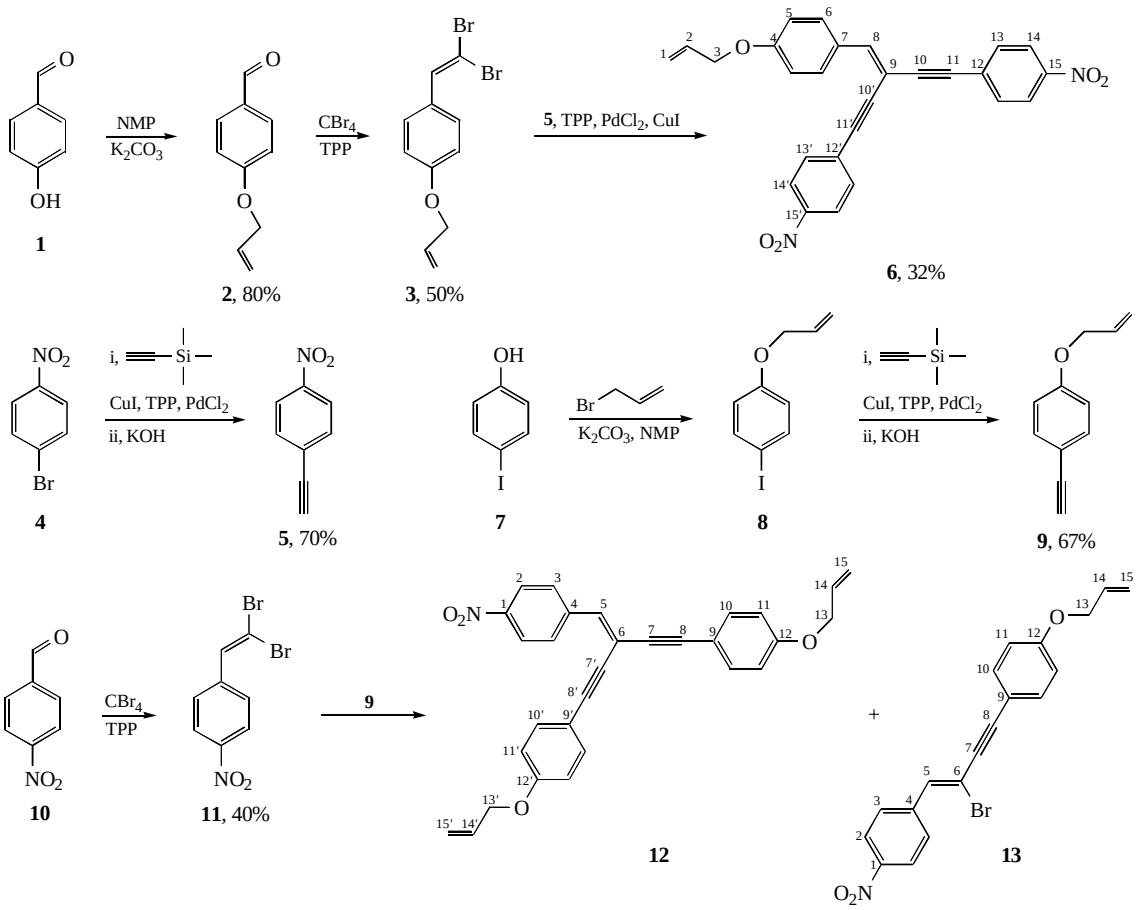
4-*Allyloxyiodobenzene* **8**: ^{1}H NMR, δ: 7.52 (d, 2H, *ortho* to I, *J* 9.0 Hz), 6.67 (d, 2H, *meta* to I, *J* 9.0 Hz), 6.07–5.94 (m, 1H, =CH–), 5.41–5.25 (m, 2H, $=CH_2$), 4.48 (td, 2H, *J* 1.5 Hz, *J* 5.1 Hz).

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*-β,β-*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*-β,β-*di*(*ethynyl-4′-allyloxyphenyl*)*styrene* **12** and 4-*nitro*-β-*bromo*-β-(*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}).



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 π-electron system as followed by long-wave absorption maxima (Table 1).

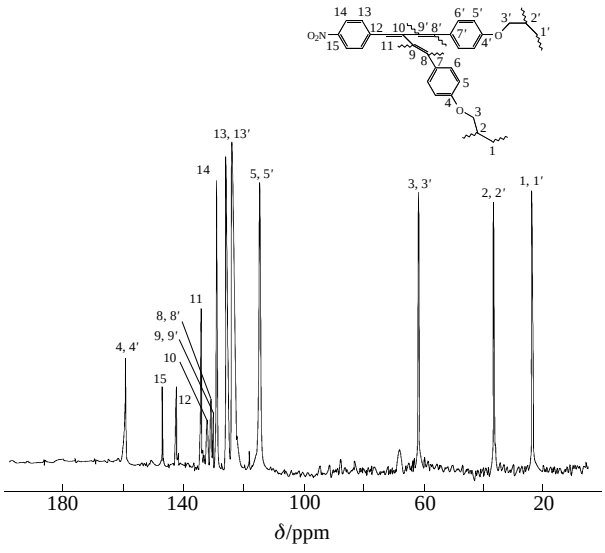
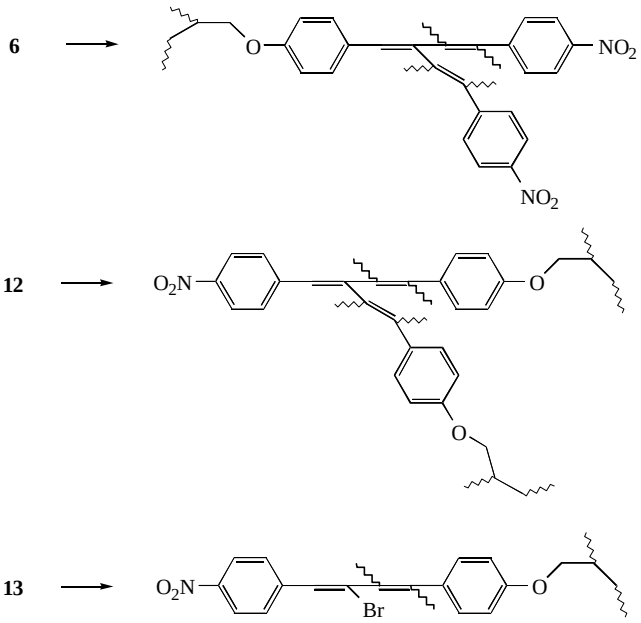


Figure 1 Solid-state NMR spectra of poly-**12** (^{1}H 90° pulse width 5 μs, cross-polarisation contact time 2 ms, spinning frequency 4 kHz).

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 β,β-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.

This work was supported by a grant from DGAPA (Direccion General de Asuntos del Personal Academico) with contract no. IN102197. Thanks are also due to M. A. Canseco, R. Gaviño, C. Vazquez and D. Rao for their assistance with the UV spectroscopy, NMR analysis, thermal analysis and NLO measurements, respectively.

References

1 H. Nalwa, *Adv. Mater.*, 1993, **5**, 341.
2 S. Fomine, A. Pineda, T. Ogawa, R. Perez and M. Sotelo, *Polym. J.*, 1995, **27**, 712.
3 S. Fomine, L. Fomina, H. Quiroz, J. M. Mendez and T. Ogawa, *Polym. J.*, 1995, **27**, 1085.
4 M. Tlenkopatchev, S. Fomine, E. Miranda, L. Fomina and T. Ogawa, *Polym. J.*, 1995, **27**, 1173.
5 S. Fomine, M. Marin, L. Fomina, R. Salcedo, E. Sansores, J. M. Mendez, C. F. Jimenez and T. Ogawa, *Polym. J.*, 1996, **28**, 641.
6 S. Fomine, C. Sánches, L. Fomina, J. C. Alonso and T. Ogawa, *Macromol. Chem. Phys.*, 1996, **197**, 3667.
7 L. Fomina, H. Allier, S. Fomine, R. Salcedo and T. Ogawa, *Polym. J.*, 1995, **27**, 591.
8 P. Beltrame, C. Veglio and M. Simonetta, *J. Chem. Soc., B*, 1967, 867.
9 L. Toldy, T. Nógrádi, L. Vargha and J. Koczka, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 303.
10 D. Matheson and H. McCombie, *J. Chem. Soc.*, 1931, 1103.

Received: Cambridge, 20th January 1998
Moscow, 18th March 1998; Com. 8/00531A