# An Improved Synthesis of Polyacetylene

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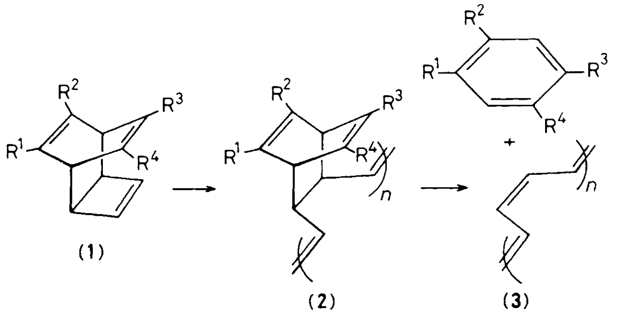
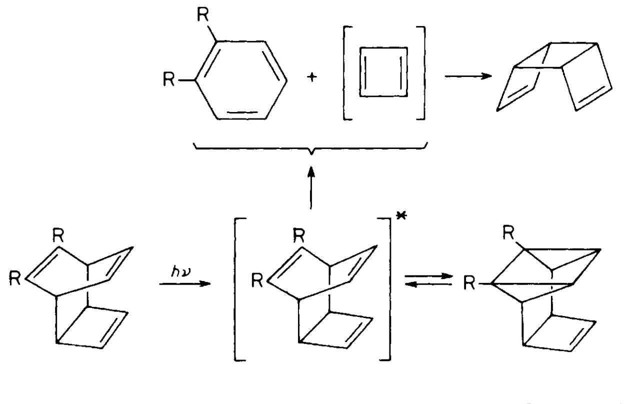
Ring-opening metathesis polymerization of 3,6-bis(trifluoromethyl)pentacyclo[6.2.0.0$^{2,4}$.0$^{3,6}$.0$^{5,7}$]dec-9-ene gives a soluble polymer which is stable at room temperature and is converted into hexafluoroxylene and polyacetylene on heating.

Conjugated polymers usually display insulator or poor semiconductor behaviour, but often they can be reversibly modified by electron-transfer reactions to provide materials which display conductivities characteristic of n- or p-type semi-conductors or metals depending on the kind and extent of modification.[1] Polyacetylene is the paradigm for this field of research and the overwhelming majority of studies have been carried out on a material produced by direct polymerization of acetylene using a technique first described by Shirakawa.[2] This material, 'Shirakawa polyacetylene,' is usually obtained in the form of an open fibrillar mat with a density of *ca.* 0.4 g cm$^{-3}$ and variable amounts of catalyst residue[1,3] which may have important effects on the observed properties of the material.[4] During the last few years we have developed an alternative effective two-stage synthesis of polyacetylene *via* a soluble precursor polymer (Scheme 1).[5—7] This approach allows the problems of regulating the polymer morphology and purity to be tackled. It is now clear that the material produced by this route, 'Durham polyacetylene,' may be obtained in a range of morphologies and densities dependent on the experimental conditions adopted for the conversion of prepolymers (**2**) into polyacetylene (**3**); particularly noteworthy is the access provided to continuous solid films with densities greater than 1 g cm$^{-3}$ and a range of degrees of crystalline order.[8—11]



**Scheme 1.** A two-stage route to polyacetylene, see refs. 5—7.

**a**; $R^1 = R^2 = R^3 = R^4 = H$
**b**; $R^1 = R^2 = CF_3$, $R^3 = R^4 = H$
**c**; $R^1 = R^2 = CO_2Me$, $R^3 = R^4 = H$
**d**; $R^1,R^2$ = benzo; $R^3 = R^4 = H$
**e**; $R^1,R^2 = R^3,R^4$ = benzo

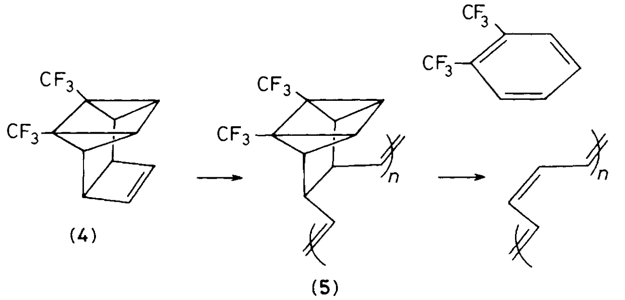


**Scheme 2.** Summary of the photochemistry of the tricyclo[4.2.2.0$^{2,5}$]-deca-3,7,9-triene system, see refs. 13—16.

The most conveniently synthesised of the monomers indicated in Scheme 1 is (**1b**), which may be obtained in high yield in a single step.[12] Unfortunately the pre-polymer (**2b**) obtained from the ring-opening polymerization of (**1b**) is relatively unstable with respect to thermal conversion into hexafluoroxylene and polyacetylene, having a half life of *ca.* 20 h at 20 °C,[7] and is consequently somewhat inconvenient to handle. Precursor polymer (**2c**) has a similar stability to (**2b**) but (**2a**) is less stable. Polymers (**2d**) and (**2e**) have greater thermal stabilities than (**2a, b,** or **c**). Polymer (**2d**) is indefinitely stable at room temperature, but may be converted into polyacetylene and naphthalene at a convenient temperature.[7] Unfortunately the monomer (**1d**) is not as easily made as (**1b**) and the eliminated naphthalene is not as easily removed from the polyacetylene as hexafluoroxylene.

We report here a modification of our original route which uses the readily accessible monomer (**1b**) and overcomes the problem of the relative instability of precursor polymer (**2b**). The photochemistry of the tricyclo[4.2.2.0$^{2,5}$]deca-3,7,9-triene system has received considerable attention[13—16] and a summary of the overall picture is shown in Scheme 2. In most cases the 3,6-disubstituted pentacyclo[6.2.0.0$^{2,4}$.0$^{3,6}$.0$^{5,7}$]dec-9-enes produced by a $2_\pi + 2_\pi$ addition are only short-lived species and the predominant products arise *via* elimination of cyclobutadiene, but Liu[13] reported that the bis-trifluoromethyl analogue is stable, which is consistent with the well established tendency for perfluoroalkyl groups to stabilize compounds containing small rings.[17] We have now isolated and purified 3,6-bis(trifluoromethyl)pentacyclo-[6.2.0.0$^{2,4}$.0$^{3,6}$.0$^{5,7}$]dec-9-ene (**4**) and used it as a monomer for a modified two-stage synthesis of polyacetylene (Scheme 3).

Irradiation of (**1b**) (3 days; 254 nm; Rayonet 208 Photochemical Reactor) in pentane gave a mixture of (**4**) and (**1b**) in a 85 : 15 ratio as the only soluble products. Low-temperature crystallization from pentane gave (**4**) in 50% recovered yield as a white solid, m.p. 46 °C, with the expected analytical and spectroscopic characteristics. The alkene (**4**) can be poly-



**Scheme 3.** A modified two-stage route to polyacetylene.

merized by typical metathesis catalysts [*e.g.* $WCl_6$–$Me_4Sn$ (1 : 2) in PhCl] to give polymer (**5**) which is relatively stable at room temperature, and thin films of (**5**) cast from acetone solution can be conveniently handled at room temperature and converted into polyacetylene by heating at 75 °C. As expected there is considerable strain energy stored in polymer (**5**), which is only stable by virtue of the fact that its thermal reversion to (**2b**) is symmetry-forbidden; the conversion of (**5**) into polyacetylene should consequently only be undertaken for *thin* films of (**5**). *Conversion of* (**5**) *in the bulk has been observed to be sufficiently exothermic to give explosions, so potential users of this route are advised to proceed with appropriate caution.*

This simple modification of our two-stage route to polyacetylene retains all the advantages discussed previously while overcoming the inconvenience of handling the pre-polymer (**2b**) at low temperature.

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