

# polymer communications

## A new synthesis of poly(acetylene)

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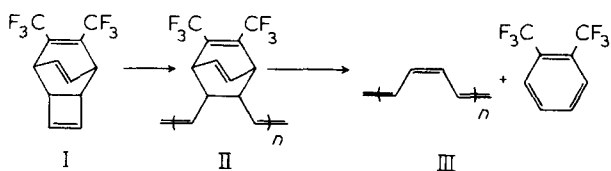
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Highly conjugated polymers have been the subject of considerable interest recently. Part of the reason for this interest stems from the observation that some of these materials display the properties of semi-conductors or of 'organic metals'. A very wide range of structures have been investigated<sup>1</sup> including poly(thiazyl),<sup>2</sup> poly(tetrathiafulvalene)s<sup>3</sup>, modified poly(vinyl ketone)s<sup>4</sup>, poly(pyrrole)<sup>5</sup>, and poly(diacetylene)s<sup>6-8</sup>. Poly(acetylene) may be regarded as the simplest example of a polyconjugated organic material; it and its derivatives have been the subject of many investigations. Poly(acetylene) is not a recent discovery; its synthesis via acetylene polymerization was described by Natta over twenty years ago<sup>9</sup>, and, even earlier, Marvel had proposed that it was the product of both the base catalysed and the thermal elimination of hydrogen chloride from poly(vinyl chloride)<sup>10,11</sup>. A large number of investigations into both these routes to polyacetylene have been described. Studies of the dehydrochlorination of poly(vinyl chloride) have generally concentrated on the mechanism of the reaction and methods for preventing its occurrence rather than the preparation of well-characterized poly(acetylenes)<sup>12</sup>; whereas reasonably well-characterized products have been obtained by direct polymerization of acetylene<sup>13-16</sup>. The electrical properties of poly(acetylene) have attracted particular attention. The polymer is a semi-conductor<sup>17</sup>, which shows a dramatic increase in conductivity when it interacts with either electron attracting<sup>18-22</sup> or electron donor<sup>23</sup> species. Although it excites so much interest, its apparent total insolubility and sensitivity to atmospheric oxidation impose considerable practical difficulties for the would-be investigator. The objective of the research communicated here is the synthesis of a soluble, stable, and well-characterized polymer which could be converted to poly(acetylene) where and when required. This communication gives the initial results from this project.

The first route chosen is shown below. The monomer 7,8-bis(trifluoromethyl)tricyclo[4,2,2,0<sup>2,5</sup>] deca-3,7,9-triene (I), is a compound<sup>24,25</sup> readily prepared in ~80% yield by the thermal reaction between hexafluorobut-2-yne and cyclooctatetraene at 120°C. The proposed metathesis ring-opening polymerization of monomer (I) could, in principle, occur at any of its three double bonds. However, in our earlier studies of trifluoromethyl substituted bicyclo[2,2,1] hepta-2,5-dienes the substituted double bonds had not been found to enter into metathesis reactions with any of a variety of active catalysts<sup>26,27,28</sup>. Also, we have found that attempts to effect the ring-opening polymerization of 2,3-bis(trifluoromethyl)bicyclo[2,2,2] octa-2,5-diene failed and so, since there appear to be no fully authenticated examples of



ring-opening polymerization at double bonds in unstrained six-membered rings, it seemed reasonable to assume that ring opening polymerization, if it occurred at all, would involve only the cyclobutene ring. With these considerations in mind the polymerization of monomer (I) was attempted using both  $WCl_6:(C_6H_5)_4Sn$  (1:2) and  $TiCl_4:(C_2H_5)_3Al$  (1:2) catalyst systems, the former gives roughly equal amounts of *cis* and *trans* main chain double bonds<sup>27</sup> whereas the latter gives predominantly *trans* stereochemistry<sup>29</sup>. Toluene was the solvent for both catalyst systems and polymerization occurred readily. When the reaction mixtures became viscous, the polymerizations were terminated by addition of methanol which also caused the precipitation of the polymer. In both cases, a fawn coloured granular product was obtained which was soluble in acetone and in chloroform. This polymer decomposed spontaneously on standing in the dark under an atmosphere of dry nitrogen (glove box port), and more rapidly in solution. The decomposition was accompanied by a sequence of colour changes from yellow, through orange, red and brown to eventually yield a black material with a metallic lustre. A sample of the raw polymer (II) left in the dark at room temperature for 3 days gave the black product and a colourless liquid identified by mass spectroscopy, <sup>1</sup>H and <sup>19</sup>F n.m.r. and infra-red spectroscopy as 1,2-bis(trifluoromethyl)benzene.

The decomposition of polymer (II) occurred much more easily than we had anticipated; nevertheless, it was possible to obtain elemental analysis figures (found: C, 55.1; H, 3.2; F, 41.7%; calculated for  $(C_{12}H_8F_6)_n$ : C, 54.1; H, 3.0; F, 42.9) and an infrared spectrum of a film cast from acetone which were in accord with the assigned structure. The analytical figures confirm that the initial polymer is a homopolymer of (I), the sample was almost certainly contaminated with traces of solvent and this accounts for the slightly high figures for carbon and hydrogen analyses and the low figure for fluorine analysis; unfortunately, prolonged pumping under vacuum was precluded since it promoted the decomposition of the material. The infra-red spectrum of polymer (II) (spectrum I, Figure 1) showed a weak band at  $1680\text{ cm}^{-1}$ .  $(-CF_3)C=C(CF_3)-$  and strong bands at 1293, 1190 and  $1142\text{ cm}^{-1}$  (C-F). The polymeric product was examined by infra-red spectroscopy and elemental analysis at various

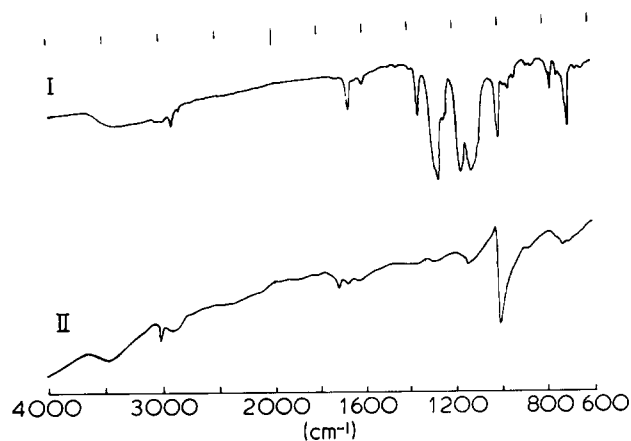


Figure 1 Infrared spectra of polymers II and III.

stages in its decomposition; in the infra-red spectra the bands referred to above gradually diminished in intensity, to be replaced by two new bands, an intense band at  $1002\text{ cm}^{-1}$  (*trans* olefinic) and a weak signal at  $709\text{ cm}^{-1}$  (*cis* olefinic?). The elemental analyses showed a gradually decreasing fluorine content and increasing carbon content with the carbon: hydrogen ratio tending to 1:1. In a typical experiment, the initial fawn polymer (II) gave in the dark a granular lustrous black material after five days which still contained a significant proportion of fluorine. In an attempt to complete the elimination of 1,2-bis(trifluoromethyl)benzene, this material was heated under vacuum (0.01 mm Hg) at  $150^\circ\text{C}$  for 5 h. At this stage, the analysis figures were C, 86.1, H, 7.9 and F, 5.7%; poly(acetylene) (III) requires C, 92.3; H, 7.7%. The sample was heated under vacuum at  $210^\circ\text{C}$  for a further period of 3 h, when the measured percentage of carbon rose to 90.4. There was no change in the appearance of the lustrous black granular product during this heating. The infra-red spectrum of the final product (spectrum II, Figure 1) shows a small sharp peak at  $3005\text{ cm}^{-1}$  (vinylic C—H) and an intense band at  $1002\text{ cm}^{-1}$  (*trans*vinylic groups). The spectrum is essentially the same as the published spectrum for *trans*poly(acetylene)<sup>14</sup>. The weak band at  $709\text{ cm}^{-1}$  might be indicative of some *cis* vinylic groups, but this seems unlikely since it is well established that *cis*—*trans* isomerization of polyacetylene occurs even at  $-30^\circ$ <sup>14,30</sup>. The Raman spectrum<sup>31</sup> of the product obtained in this work was also effectively the same as that of the published spectrum of *trans*poly(acetylene)<sup>15</sup>. The black lustrous material was susceptible to atmospheric oxidation and after a few days exposure on the laboratory bench gave a light brown product with a carbon content of 46.7%. This oxidation appears to be limited to the surface of the product, since, when some of the larger particles were broken open, the newly exposed surfaces still displayed a black metallic lustre.

The evidence presented above establishes that the proposed sequence occurs. The ease with which polymer (II) loses 1,2-bis(trifluoromethyl)benzene means that this system is too labile for convenient generation of poly(acetylene) and we are currently investigating related structures in order to find a somewhat more stable precursor. The reluctance of our product to lose all its fluorine, even on prolonged heating, might be interpreted as evidence for structural features

other than that indicated for polymer (II) (see Figure 1). However, we feel that a more likely explanation is that the last traces of the relatively large aromatic molecules which are eliminated are trapped within the matrix of the poly(acetylene) sample. The impermeability of poly(acetylene) is evident by the fact that oxidation by atmospheric oxygen was limited to the outer layers of the material even after prolonged exposure ( $\sim 1$  month).

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