

New routes to conjugated polymers: 1. A two step route to polyacetylene

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This paper describes routes to poly(acetylene) which involve the synthesis of soluble precursor polymers which may be purified and subsequently converted to poly(acetylene) via a symmetry allowed thermal elimination reaction. Poly(acetylene) produced in this way is free from catalyst residues and other impurities. The method allows the production of poly(acetylene) in the form of continuous uniform and featureless films as opposed to the disordered fibrillar mat morphology obtained as a result of the direct polymerization of acetylene.

Keywords Poly(acetylene); syntheses; catalyst-free; continuous film

INTRODUCTION

Poly(acetylene) is a material which has attracted a great deal of interest in the last few years and has been the subject of several recent reviews¹⁻⁴. Most of the work reported has been concerned with materials produced directly from acetylene using techniques first established by Shirakawa⁵ and Luttinger⁶. The vast majority of papers on poly(acetylene) have been concerned with either structural studies or changes in electrical conductivity brought about by chemical treatments, which are often described as 'doping'.

Acetylene has a long established, voluminous and interesting chemistry⁷, and it is reasonable to expect that its polymerization will be accompanied by a variety of side reactions; thus, dimerization and formation of benzene and cyclooctatetraene, cycloadditions and isomerizations, and further reactions of the initial products, might be anticipated. In attempts to remove catalyst residues and impurities produced by such side reactions different groups of workers have adopted a variety of purification procedures. However, there is no universally accepted 'clean up' procedure and consequently it is likely that different studies of the physics and chemistry of either Shirakawa or Luttinger poly(acetylene), although formally concerned with the same materials, are in practice dealing with different forms of poly(acetylene). The variable chemical contamination is a generally unacknowledged factor which should properly be added to the acknowledged structural variations arising from *cis-trans* isomerization. The former is, of course, much more difficult to characterize quantitatively than the latter. The preceding observations could account for the apparent anomalies between the studies reported by different groups. The problems indicated above are compounded by the fact that poly(acetylene) is insoluble, infusible and susceptible to fairly rapid atmospheric degradation. Its insolubility and infusibility not only make purification difficult, but also preclude most

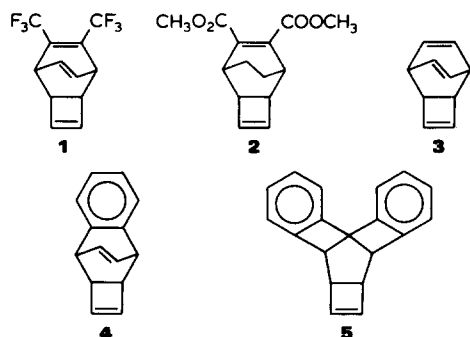
conventional fabrication methods and procedures for modifying the polymer's bulk morphology. Despite the practical difficulties indicated above poly(acetylene) continues to excite considerable interest, it therefore seems worthwhile to address the problem of producing high purity material by methods which will allow convenient fabrication and control of the bulk morphology.

We see essentially three methods of tackling this problem. The first would involve the production of a fully processable form of poly(acetylene); and, for example, scientists from the Bayer company recently reported work directed to this objective⁸. The second route requires the synthesis of a stable processable polymer which is capable of either thermal or photochemical isomerization to poly(acetylene); to the best of our knowledge such a route is not presently available. The third approach again requires the synthesis of a stable precursor polymer which in this case is capable of being converted to poly(acetylene) via a thermally or photochemically promoted elimination reaction. In the latter two approaches the possibility of rigorous purification of the precursor polymers prior to production of poly(acetylene) allows, at least in principle, the production of high purity material. In the eliminative route the conversion step has to be quantitative and the eliminated compounds have to be easily and totally removed from the product. In this discussion we have referred exclusively to poly(acetylene) but it is clear that a completely analogous analysis applies to syntheses of other conjugated polymers such as, for example, poly(phenylene)s and poly(arylene vinylene)s. In this paper we describe work directed to the thermal eliminative route to poly(acetylene), in an earlier communication we outlined the chemistry of the process⁹, although at that time we were not optimistic about the value of this approach in producing high purity poly(acetylene). We now report further work which establishes that this route provides access to high purity material and to a morphology not previously encountered.

EXPERIMENTAL

Monomers

The monomers used in this work: 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene(1)¹⁰, dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene-7,8-dicarboxylate(2)¹¹, tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene(3)¹², 7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene(4)¹³, and 7,8,9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene(5)¹⁴, were prepared and purified by the methods described in the references cited. All five monomers were single components on standard chromatographic analysis, had correct melting or boiling points and elemental analyses, and their spectra (i.r., n.m.r. and mass) were in agreement with those described previously.

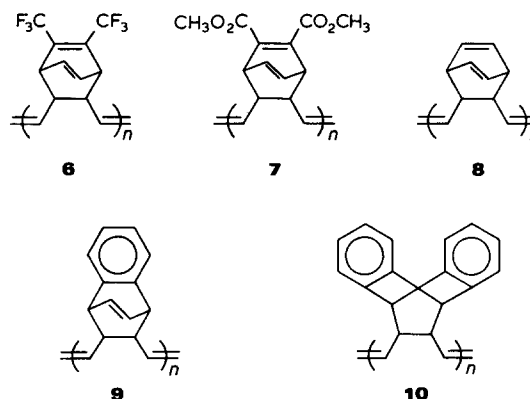


Polymerizations

Monomers 1 to 5 were polymerized via ring opening at the cyclobutene unit's double bond using a metathesis catalyst prepared from tetramethyltin and tungsten hexachloride. Success in these reactions required that reagents, solvents and apparatus were rigorously dried and that oxygen was excluded. In practice we have found that freshly prepared tungsten hexachloride¹⁵ was generally satisfactory. Chlorobenzene proved to be a suitable solvent, it was fractionally distilled from P₂O₅ and degassed prior to use. All manipulations were conducted under a dry nitrogen atmosphere (<8 ppm O₂). Typically the catalyst was generated by adding neat tetramethyltin to a stirred solution of tungsten hexachloride in chlorobenzene. The mixture was stirred at room temperature for five minutes during which time a colour change from intense blue-black to red-brown was observed, the monomer was then added in one portion either neat [(1), (2) and (3)] or as a solution in chlorobenzene [(4) and (5)]. The mixtures became viscous as polymerization occurred and the reactions were terminated by the addition of methanol. The polymerizations reported here have been repeated many times, however it has to be acknowledged that the reactions appear to be sensitive to relatively small temperature changes and to the age of the catalyst solution, and that variable induction periods and

occasional unexplained failures have been observed. The polymers were precipitated by addition of excess methanol and recovered by filtration, the solid products were washed with methanol and dried at 0°C under reduced pressure (10⁻³ mm Hg). Purification was achieved by repeated reprecipitation from cold acetone into cold methanol. Polymer samples were dried under vacuum at 0°C and stored under vacuum or dry nitrogen at temperatures < -20°C. Typical illustrative examples of polymerizations are summarized in Table 1.

The products of reaction of monomers (1)–(5) with metathesis catalysts are expected to have the structures shown below. In all cases there was a marked increase in solution viscosity during the polymerization reaction, and solutions of the purified products all displayed the high viscosity at low concentration typical of polymeric materials. The thermal instability of products (6), (7) and



(8) (see later) has so far precluded the use of conventional solution phase characterization techniques with these materials. However, gel permeation chromatography analysis of (9) (μ -styrigel 10⁶ Å column set, THF solvent) indicated that the material had a molecular weight distribution $M_w/M_n > 4$ and the peak of the distribution curve occurred at a hydrodynamic volume slightly greater than that for a standard sample of polystyrene with $M_n = 40\,000$. Methods for obtaining reliable molecular weight data for these thermally unstable polymers are under active investigation and the results will be the subject of a later paper; however, it seems reasonable to conclude that the materials (6)–(10) are genuine polymers. All these materials, except (8), could be cast from solution to give continuous films; polymer (8) was not completely soluble and was the most difficult material to manipulate although it was thermally transformed to poly(acetylene) and benzene as expected (see later).

The infra-red spectra of monomers (1) to (5) and derived polymers (6) to (10) respectively were consistent with the structures assigned. Bands in the spectra of (6) to (10) were

Table 1 Examples of polymerizations

Monomer number	Monomer quantity g (mmoles)	WCl ₆ g (mmoles)	(CH ₃) ₄ Sn g (mmoles)	Temperature (°C)	Time (min)	% Yield after reprecipitation
1	16.1 (60.56)	0.3240 (0.815)	0.292 (1.63)	15	20	90
2	1.0 (4.34)	0.0280 (0.071)	0.025 (0.14)	20	60	95
3	1.0 (7.7)	0.0757 (0.19)	0.068 (0.38)	15	1	100 ^a
4	1.0 (5.55)	0.0738 (0.186)	0.066 (0.37)	20	2	90 ^b
5	0.3 (1.32)	0.0677 (0.17)	0.061 (0.34)	20	120	95 ^b

^a This polymer was not reprecipitated as it was not completely soluble

^b Reprecipitated from chlorobenzene into methanol

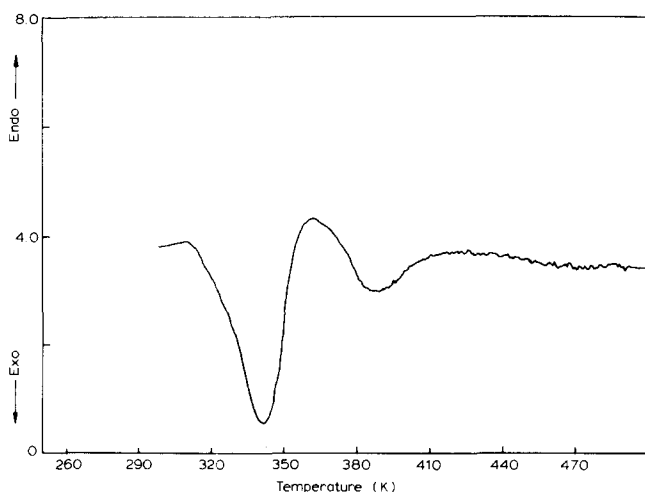
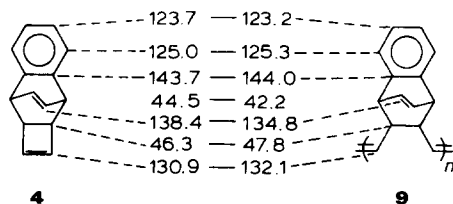


Figure 1 D.s.c. record for polymer (6) – 13.35 mg, $2.50^{\circ}\text{C min}^{-1}$

somewhat broadened as compared with the monomers, the monomer/polymer pairs showing generally similar spectra. The spectra provided evidence that polymerization occurred at the cyclobutene double bond in that weak absorptions at 1550 (1) and (4), and 1580 cm^{-1} (5) which may be assigned to the $\text{C}=\text{C}$ stretch of the cyclobutene units in the monomers are not observed in the derived polymers, (6), (9) and (10) respectively.

The thermal instability of polymers (6), (7) and (8) in solution has so far precluded recording useful ^{13}C n.m.r. spectra for these polymers. Polymer (9) had a sufficiently long life in solution for a spectrum to be recorded although the signals were rather broad and even for this relatively stable material, peaks ascribed to the eliminated naphthalene moiety were clearly evident. The monomer (4) and polymer (9) shift assignments are recorded below.

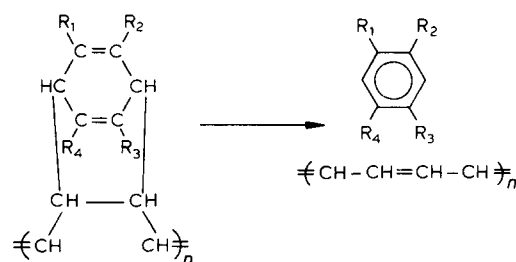


The aromatic ring carbons show only minor shift differences between the monomer and polymer spectra, the bridging vinylene and bridgehead carbons at 138.4 and 44.5 in the monomer are shifted to slightly higher field (134.8 and 42.2 ppm) in the polymer which is consistent with the relief of ring strain in this part of the molecule^{16,17}. The vinylic and sp^3 carbons of the cyclobutene unit in the monomer appear as sharp lines, whereas the signals from the analogous carbons in the polymer are very broad unresolved bands which we take as evidence that the polymer contains *cis*- and *trans*-vinylene units. The catalyst system used in these polymerizations generally produces a mixture of *cis*- and *trans*-vinylene units in approximately equal proportions¹⁷.

Transformations

Polymers (6), (7), (8), (9) and (10) undergo a thermal transformation reaction with the elimination of 1,2-bis(trifluoromethyl)benzene, dimethylphthalate, benzene, naphthalene and anthracene respectively. This symmetry allowed process is summarized in the scheme below which

also indicates the temperature ranges in which the transformations can be achieved at an experimentally convenient rate. The eliminated molecules were identified



- | | | |
|----|----------------------------------------------------------|----------------------------------------|
| 6 | ($R_1 = R_2 = \text{CF}_3, R_3 = R_4 = \text{H}$) | 50° to 120°C |
| 7 | ($R_1 = R_2 = -\text{COOCH}_3, R_3 = R_4 = \text{H}$) | 50° to 120°C |
| 8 | ($R_1 = R_3 = R_4 = \text{H}$) | 20° to 50°C |
| 9 | ($R_1, R_2 = \text{anthracene}, R_3 = R_4 = \text{H}$) | 100° to 150°C |
| 10 | ($R_1, R_2 = R_3, R_4 = \text{anthracene}$) | 175° to 200°C |

by spectroscopy (i.r., n.m.r. and mass), and the involatile residue was identified as polyacetylene (i.r. and solid state CPMA^s ^{13}C n.m.r.). This transformation reaction has been studied by differential scanning calorimetry (Perkin-Elmer DSC 2C, coupled with thermal analysis data station using the standard and kinetic software packages) the d.s.c. traces for the transformation reactions of polymers (6), (9) and (10) are recorded in Figures 1, 2 and 3. As can be seen from the Figures the temperature of onset of the elimination reaction varies with the molecular structure of the polymer; thus, 1,2-bis(trifluoromethyl)benzene began to be eliminated from (6) at about 310K , naphthalene from (9) at about 380K and anthracene from (10) at about 500K . These observations are reflected in the observed stability of the polymers. Those which transform by elimination of a benzene derivative, i.e. (6), (7) and (8), being unstable at room temperature; for example, the half life of polymer (6) at 20°C is approximately 20 h. On the other hand, polymers (9) and (10) appear to be indefinitely stable at room temperature as evidenced by their i.r. spectra being unchanged after storage at room temperature for one year.

As an illustrative example of the transformation process, polymer (6) can be obtained as a white or light tan powder which is soluble in acetone, ethylacetate and chloroform. Acetone appears to be the most efficient solvent, with a limiting solubility of about 100 g/litre . In

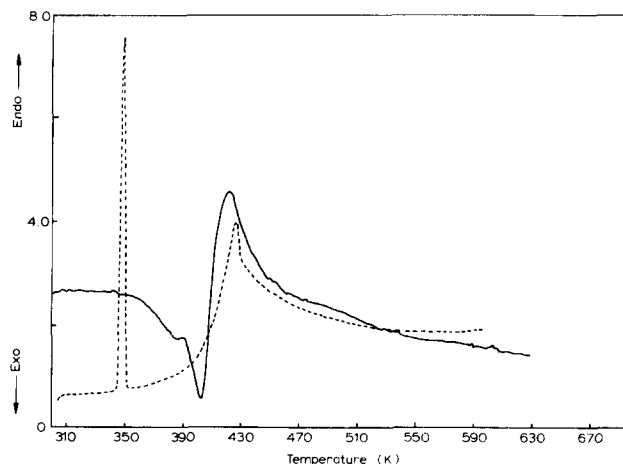


Figure 2 D.s.c. record for polymer (9) – 8.71 mg, $2.50^{\circ}\text{C min}^{-1}$. Broken line shows record for naphthalene, melting and subliming

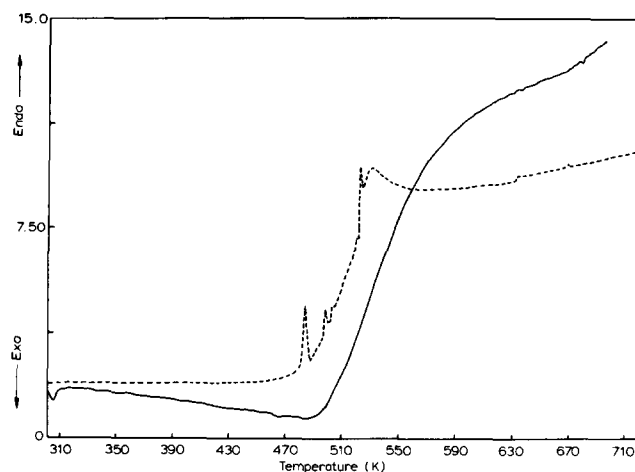


Figure 3 D.s.c. record for polymer (10) – 5.87 mg, 2.50°C min⁻¹. Broken line shows record for anthracene

such a solution or as a cast film the polymer undergoes a transformation to poly(acetylene) at a rate determined by the temperature. At room temperature, within a few hours the solution or film develops a distinctive yellow cast which deepens through orange to red. This colour darkens further and if a solution is used a fine suspension of black powder is obtained after about 20 h. If a film is used and subject to a dynamic vacuum, then the blackened film develops a silvery sheen after about the same time. The most prominent absorption bands in the infra-red spectrum of polymer (6) are those associated with the CF₃ groups, which occur at 1293, 1190 and 1142 cm⁻¹. During the transformation reaction these bands are entirely eliminated from the i.r. spectrum; we estimate that one unconverted monomer residue per 100 would have been detected. Complete conversion requires relatively thin films (≤ 100 microns) in thicker samples it is difficult to eliminate entirely the absorption bands associated with the CF₃ groups, although we believe this is associated with the difficulty of removing the 1,2-bis(trifluoromethyl)benzene from the sample rather than incomplete transformation. Raising the temperature of the transformation reaction by 5°C roughly doubles the rate of this reaction, suggesting an activation energy of about 100 kJ mol⁻¹ for the transformation reaction.

When heated from room temperature in the DSC 2C apparatus a sample of polymer (6) shows a large (ca. 8 kJ mol⁻¹) exotherm (Figure 1) associated with the transformation reaction followed by a smaller exotherm associated with the *cis/trans* isomerization. Inspection of Figures 1, 2 and 3 indicates that the exotherm associated with the elimination reaction is only clearly resolved from other thermal processes, such as isomerization, melting and sublimation, in the case of polymer (6), consequently, kinetic data was only obtained for this system. Analysis of the transformation reaction shows that it is first order with an activation energy of 100 kJ mol⁻¹. Although the activation energy confirms the earlier qualitative estimate from simple temperature dependence, it is surprising that the transformation reaction appears to be first order, implying that elimination is random and unaffected by the structure of the adjacent polymer chain.

CONCLUSIONS

The sequence of reactions described above offers a completely new synthetic route to poly(acetylene). The

two stage nature of these syntheses has several advantages over conventional methods. The first is the ability to remove catalyst residues from the polymer via conventional techniques, this allows the production of catalyst free poly(acetylene) and hence recognition of the effect of residues on electrical properties. Secondly the precursor polymers are processable, that is they can be cast as films from solution, this provides the possibility of morphological control of the precursor polymer and hence the final poly(acetylene). The poly(acetylene) produced by this route has similar molecular structure to the material prepared by conventional routes, as shown by the fact that infra-red, Raman and ¹³C n.m.r. spectra are essentially identical. The morphology produced by conversion of a free standing film is, however, totally different and electron microscopy and X-ray studies reveal no significant order¹⁸. In particular the ability to produce a thin, coherent film of poly(acetylene) is a significant development, since the material produced by direct polymerization of acetylene is a disordered fibrillar mat. The material is similar to conventional forms of poly(acetylene) in that it can be doped to similar levels of conductivity¹⁸. Detailed structural and electrical studies of poly(acetylene) produced by the methods described in this paper will be reported in subsequent publications in this series.

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