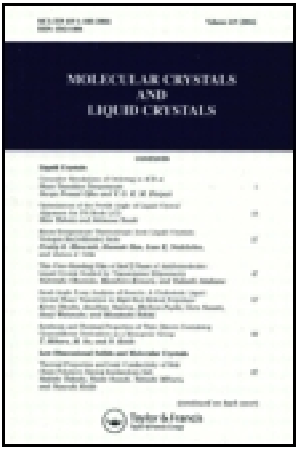


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Some Aspects of the Chemistry of the Two Step Durham Route to Polyacetylene

D. C. Bott [a], C. S. Brown [a], J. H. Edwards [b], W. J. Feast [b], D. Parker [b] & J. N. Winter [b]

[a] B. P. Research Centre, Sunbury-on-Thames, Middlesex, TW16 7LN, U.K.

[b] Durham University, Chemistry Department, South Road, Durham, DH1 3LE, U.K.

Version of record first published: 17 Oct 2011.

To cite this article: D. C. Bott, C. S. Brown, J. H. Edwards, W. J. Feast, D. Parker & J. N. Winter (1985): Some Aspects of the Chemistry of the Two Step Durham Route to Polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 9-14

To link to this article: http://dx.doi.org/10.1080/00268948508074586

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 9-14
0026-8941/85/1174-0009/$15.00/0

SOME ASPECTS OF THE CHEMISTRY OF THE TWO STEP DURHAM ROUTE TO POLYACETYLENE

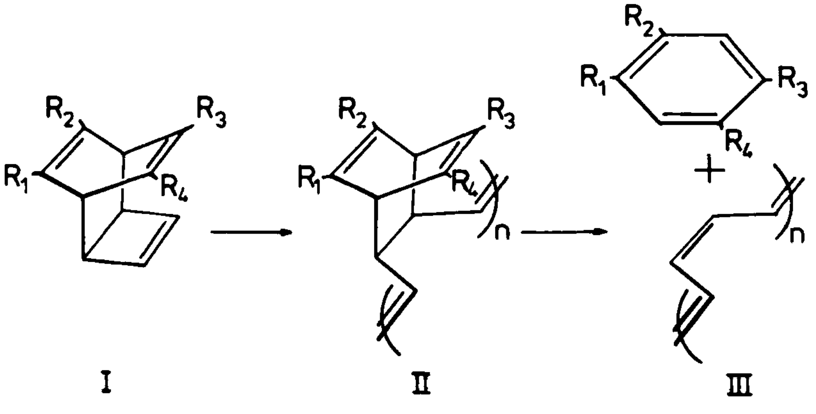
D.C. BOTT,[a] C.S. BROWN,[a] J.H. EDWARDS,[b] W.J. FEAST,[b*]
D. PARKER[b] and J.N. WINTER[b]

[a] B.P. Research Centre, Sunbury-on-Thames, Middlesex, TW16 7LN, U.K. [b] Durham University Chemistry Department, South Road, Durham, DH1 3LE, U.K.

Abstract Mechanistic aspects of the two step Durham route to polyacetylene are discussed. It is shown that a catalyst based on $MoCl_5$ gives a higher proportion of cis vinylenes in both precursor polymer and nascent polyacetylene than does a WCl_6 based system.

INTRODUCTION

Scheme 1 represents a two step route to polyacetylene which we have developed during the last few years.[1-3] This approach has advantages over direct polymerization of acetylene; for example, polymers II are soluble and consequently may be purified by



SCHEME 1 A two step route to polyacetylene

conventional procedures prior to conversion to polyacetylene III. Solvent cast films or fibres of II undergo a thermal elimination of an aromatic compound to generate III which is isomerized to trans-polyacetylene under the usual conditions adopted for the conversion reaction. It is now clear as a result of our own work[2-4] and that of others[5-7] that polyacetylene produced by this route differs from the materials previously available. It is also recognized that morphological details of polyacetylene samples produced via the Durham route are dependant on the conversion protocol adopted, and that continuous solids (films, fibres, etc.) with a range of crystallinities and anisotropies can be produced rather than the fibrular mats previously available. In Scheme 1 structure II represents a family of polymers and it is reasonable to expect that variations in structural details will have an influence on the properties of individual members of this family. The combined effects of four variables have to be considered: (i) the nature of the substituents $R_1 \rightarrow R_4$, (ii) the proportion and distribution of cis and trans vinylene units, (iii) the proportion and distribution of meso and racemic dyads, and (iv) the value and distribution of the degree of polymerization (n in Scheme 1). Most of the work so far reported on this route to polyacetylene has used a catalyst system based on $WCl_6/(CH_3)_4Sn$ for the initial ring opening metathesis polymerization stage and a monomer I in which $R_1 = R_2 = CF_3$- and $R_3 = R_4 =$ H-, this choice imposes some practical inconvenience since polymer II with these substituents is unstable at room temperature. We have shown that variation of substituents can have a profound effect on the stability of II; for example, when $R_1/R_2 = C_4H_4$ (1,4-butadienylene) and $R_3 = R_4 =$ H II is stable at room temperature and conveniently converted to polyacetylene and naphthalene at ca. 380 to 400K, whereas when R_1/R_2 and R_3/R_4 are both 1,4-butadienylene polymer II does not undergo conversion to anthracene and polyacetylene until ca. 500K, an unsatisfactorily high temperature.[2,3]

In this paper we present some comments relating to points (ii) and (iii) above, information relating to point (iv) is reported elsewhere.[8]

RESULTS AND DISCUSSION

The first step in the synthesis under consideration here (Scheme 1) is a *ring-opening metathesis polymerization* of a substituted cyclobutene, this is a special case of the more general process of ring-opening polymerization of cycloalkenes which has been the subject of many detailed studies during the last twenty years.[9] It is now clear that for such polymerizations the outcome, with respect to polymer chain microstructure is a sensitive function of monomer structure and concentration, reaction temperature, solvent and catalyst. Indeed the tacticity of a polymer produced by this method may change as the reaction proceeds and the monomer concentration drops, and relatively small structural changes in the monomer can have a marked effect on the reaction outcome. Considerations such as these make generalizations about the likely result of a metathesis ring-opening hazardous, never-the-less we have found in the polymerization of a series of polycyclic polyenes which have structural features in common with II that the catalyst system $WCl_6/(CH_3)_4Sn$ tends to give atactic polymers with a 1:1 cis:trans vinylene ratio, whereas $MoCl_5/(CH_3)_4Sn$ catalysts give partially stereoregular polymers with a relatively high proportion of cis vinylenes.[10] We have therefore examined the polymerization of I (where $R_1 = R_2 = CF_3-$ and $R_3 = R_4 = H-$) with both WCl_6 and $MoCl_5$ based catalysts and monitored the relative cis vinylene content by measuring the relative size of the cis → trans isomerization peak in the differential scanning calorimetry record of the conversion process II to III.

The conversion step II to III (Scheme 1) is a symmetry allowed ground state process as is demonstrated by the lack of any crossing of the non-bonding level (broken line) in the orbital correlation diagram (Figure 1),[11] in which orbitals transformed are classified with respect to the plane of symmetry (dotted line) maintained throughout the process. The polymerizations which

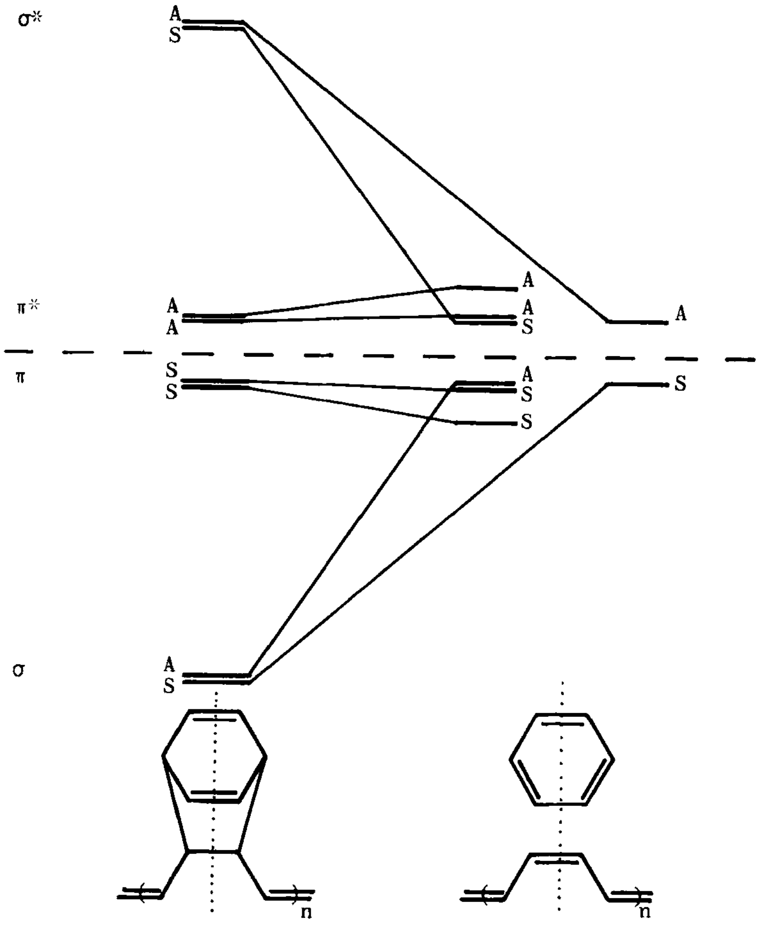


FIGURE 1 Orbital correlation diagram for the II → III conversion process

produce II give a ratio of cis:trans vinylene units dependant on the details of the particular reaction but <u>all newly formed</u>

vinylenes during the II to III stage must be cis; consequently, since we have previously shown that the exotherm associated with the elimination reaction can be resolved from that associated with the cis to trans isomerization process,[3] the ratio of the isomerization peaks in the DSC trace of different samples of II should give an indication of the proportion of cis vinylenes in the nascent polyacetylene and hence in the precursor polymers II.

Two samples of II were prepared and purified by the method described previously,[3] sample W was made with catalyst WCl_6/$(CH_3)_4Sn$ and sample Mo with $MoCl_5/(CH_3)_4Sn$, in all other respects the samples were treated identically. The magnitude of the isomerization exotherm was measured using a Perkin-Elmer DSCII instrument and a protocol in which the sample was heated at 10 $K.min^{-1}$ to 371 K then cooled to room temperature prior to recording the cis to trans isomerization peak. Sample W showed an isomerization peak exothermic to the extent of 57.1 $J.g^{-1}$, whereas sample Mo had a value 63.7 $J.g^{-1}$. The ratio of the isomerization exotherms for sample W and sample Mo is therefore 57.1/63.7, i.e. 0.9. If we assume that sample W has a 1:1 cis: trans vinylene ratio (as is typically the case for polymerizations with $WCl_6/(CH_3)_4Sn$) it follows that the proportion of cis units in the nascent polyacetylene from this precursor will be 0.75, and consequently the proportion of cis units in the nascent polyacetylene derived from sample Mo is given by 0.75/0.9, i.e. 0.83, which in turn was derived from a 33:17 cis:trans vinylene ratio in the Mo derived pre-polymer II. Thus, this admittedly simple analysis leads to the conclusion that if the WCl_6 based catalyst gives a 1:1 cis:trans vinylene ratio in pre-polymer II, then the $MoCl_5$ based catalyst gives a 2:1 preponderance of cis units. This result is consistent with the general trends observed in metathesis ring-opening polymerizations[9,10] suggesting that despite its relative complexity and steric congestion monomer I is behaving in the expected manner during the polymerization step leading to II.

ACKNOWLEDGEMENTS

The Durham component of this work was supported by an SERC/BP Co-operative Award (J.H.E.) and a BP Extra-Mural Research Agreement (D.P. and J.N.W.).

REFERENCES

1. J.H. Edwards and W.J. Feast, Polymer, 21, 595 (1980).
2. D.C. Bott, C.K. Chai, J.H. Edwards, W.J. Feast, R.H. Friend and M.E. Horton, J. Physique Colloque C-3, Suppl. 6, 44, C3-143 (1983).
3. J.H. Edwards, W.J. Feast and D.C. Bott, Polymer, 25, 395 (1984).
4. D. White and D.C. Bott, Polymer Comm., 25, 98 (1984).
5. G. Leising, Polymer Comm., 25, 201 (1984) and Polymer Bulletin, 11, 401 (1984).
6. H. Kahlert and G. Leising, reported at ICSM84, Abano Terme, Italy, June 1984.
7. G. Wegner, G. Lieser, et al, reported at ICSM84, Abano Terme, Italy, June 1984; see also ACS Polymer Preprints for 188th ACS National Meeting, Philadelphia, 1984.
8. K. Harper and P.G. James, reported at ICSM84, Abano Terme, Italy, June 1984.
9. For a recent authoritative survey and discussion see K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983.
10. A.B. Alimuniar, J.H. Edwards and W.J. Feast, J. Mol. Cat., submitted; and A.B. Alimuniar, P.M. Blackmore, I.S. Millichamp, L.A. Shahada and W.J. Feast, unpublished results.
11. R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, 1970.