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

Molecular Weight Distributions of Durham Polyacetylene Precursor Polymers

Kevin Harper [a] & Peter G. James [a]
[a] BP Research Centre, Chertsey Road, Sunbury-on-Thames, England

Version of record first published: 17 Oct 2011.

To cite this article: Kevin Harper & Peter G. James (1985): Molecular Weight Distributions of Durham Polyacetylene Precursor Polymers, Molecular Crystals and Liquid Crystals, 117:1, 55-58

To link to this article: http://dx.doi.org/10.1080/00268948508074595

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 55-58
0026-8941/85/1174-0055/$10.00/0

Printed in the United States of America

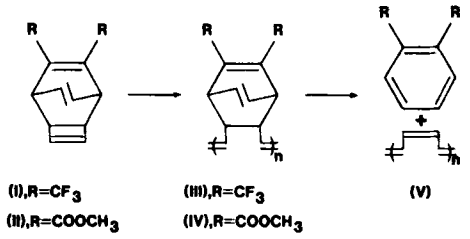
MOLECULAR WEIGHT DISTRIBUTIONS OF DURHAM POLYACETYLENE PRECURSOR POLYMERS

KEVIN HARPER AND PETER G. JAMES
BP Research Centre, Chertsey Road, Sunbury-on-Thames, ENGLAND.

Abstract: A low temperature gel permeation chromatography system has been developed and used to obtain the molecular weight distributions of a series of Durham polyacetylene precursor polymers.

INTRODUCTION

The Durham route to polyacetylene (1) is summarised in Scheme 1.



Scheme 1

Monomers (I) or (II) are ring-open polymerised using typical metathesis catalysts to give Durham precursor polymers (III) or (IV). These polymers are thermally unstable and may be controllably transformed to give polyacetylene (V). However, their thermal instability has so far precluded the use of conventional solution-phase techniques for their characterisation. The molecular weight distributions of samples of Durham polymers (III) and (IV) have recently been obtained using low temperature gel permeation chromatography (GPC) as outlined below.

EXPERIMENTAL

The GPC apparatus used is represented schematically in Figure 1.

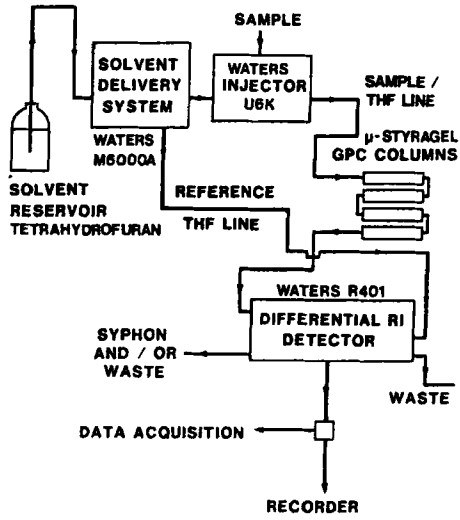


Figure 1: Schematic experimental layout for gel permeation chromatography

GPC relies on the ability of porous supports (μ-styragel)(2) to separate polymer molecules by virtue of their size or hydrodynamic volume. A condition of the technique is that the polymer must be soluble in the eluent solvent. The columns were calibrated with standards (monodisperse polystyrene) of known molecular weight so that a distribution function in terms of molecular weight could be obtained. The GPC apparatus (excluding the data acquisition and recorder units) was situated in a cold room with an ambient temperature of -17°C. At this temperature reproducible GPC distribution curves were obtained.

RESULTS AND DISCUSSION

A typical GPC distribution curve for a sample of Durham polymer (III) is shown in Figure 2. A variety of samples were studied. Examples of some of the results obtained are given in Table 1. "Polystyrene equivalent" weight-average molecular weights ranged from 200,000 to 500,000 depending upon the polymerisation conditions, indicating that Durham polymer is a genuine high molecular weight polymer.

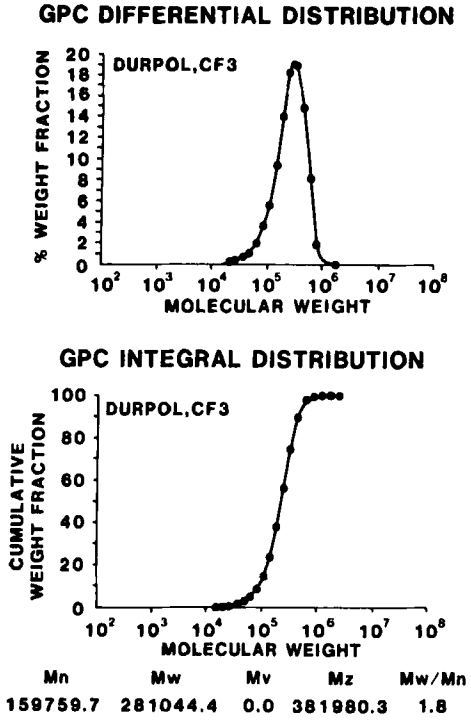


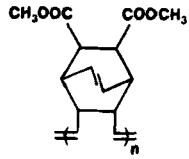
Figure 2. GPC distribution curve for a sample of Durham polymer

POLYMER	MOLE RATIOS(a) Monomer:Solvent	Mw	Mn	Mw/Mn
(III)	100:1075	281,000	160,000	1.8
(III)	144:1014	412,000	179,000	2.3
(III)	100:750	389,000	156,000	2.5
(III)	100:1000	256,000	92,000	2.8
(III)(b)	100:750	269,000	104,000	2.6
(IV)	100:2000	402,000	184,000	2.2

(a) Relative to WCl_6($MoCl_5$):$SnMe_4$ ratio of 1:2
(b) $MoCl_5$ used

Table 1:"Polystyrene equivalent" molecular weights for a range of Durham polymers

To check the validity of the "polystyrene equivalent" molecular weights obtained by GPC, the weight-average molecular weight of a sample of the room-temperature-stable model polymer (VI) was obtained by light-scattering (3). A sample of polymer (VI) with a GPC "polystyrene-equivalent" molecular weight of 279,000 had a light-scattering molecular weight of 590,000, hence the values given in Table 1 should be corrected by multiplying by a factor of 2. These results indicate that the number of double bonds in Durham polyacetylene is as high as 7500 (4).



(VI)

CONCLUSIONS

(1) The molecular weight distributions of Durham precursor polymers have been obtained using low temperature GPC.
(2) A concurrent light-scattering experiment indicated that the "true" weight-average molecular weights of the Durham-type polymers were approximately twice the "polystyrene-equivalent" molecular weights.
(3) Durham precursor polymers are genuine high molecular weight polymers, producing initially cis polyacetylene with up to 7,500 double bonds.

ACKNOWLEDGEMENTS

The authors would like to thank British Petroleum plc. for permission to publish this work. Our thanks go also to Richard Weatherhead and Gerry Winter for preparation of samples.

REFERENCES

(1) John H. Edwards, W. James Feast and David C. Bott, POLYMER 25(3), 395 (1984).
(2) μ-styragel is a registered trademark of Waters Associates.
(3) P.M. Budd personal communication
(4) Based on the formation of cis polyacetylene according to Scheme 1.