

AN INITIAL EVALUATION OF POLY(VINYLACETYLENE) AS A CARBON FIBRE PRECURSOR.

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INTRODUCTION

Carbon and graphitic fibres are known to possess excellent mechanical properties and are much sought after materials in structural applications. A wide range of polymeric precursors have been converted into carbon fibres, and the search for a more efficient precursor and an accompanying process poses a challenge to many.

The polymer obtained from the selective polymerisation of monovinylacetylene through the vinyl group contains a saturated carbon backbone and pendant acetylenic groups. This polymer, poly(vinylacetylene), structurally resembles PAN, but has a greater reactivity and a higher carbon content. This polymer has been investigated by us as potential alternative carbon fibre precursor.

The polymerisation behaviour of monovinylacetylene and the routes used by us to synthesise the polymer will be discussed briefly. The principal aim of this work was however to study the carbonisation process for this polymer. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were used to follow the process and to optimise the overall carbon yield.

EXPERIMENTAL

Monovinylacetylene was synthesised by the catalytic dehydrohalogenation of trans-1,4-dichlorobutene as described in the literature [1]. The polymer used in our study was synthesised anionically after substitution of the acetylenic proton with lithium,

followed by reprotonation of the formed polymer.

Molecular weights were determined on a Spectra Physics AS 1000 apparatus (PSS 5 μ m, SDV 1000 Å & 10⁵ Å, Shodex RI 71, Viskotek H502).

Filaments of diameter 40 μ m were melt-spun from the obtained polymer. Diameters were measured by optical microscopy.

Infusibilisation of the obtained fibres was performed by exposure to a 300 nm UV light source in a nitrogen atmosphere, followed by thermal treatment in an oven under a flow of nitrogen up to 225°C at a rate of 1°C/min. Oxidation of the infusibilised fibres was carried out in the oven at the same temperature in an air flow. The fibres were subjected to various periods of oxidation.

Infrared spectra of poly(vinylacetylene) films cast from a THF solution of the polymer on KBr discs were recorded on a Mattson spectrometer. Infusibilisation and oxidation of the fibres were carried out under conditions similar to those employed for the fibres.

TG and DSC analyses were performed on Perkin Elmer equipment (Series 7).

RESULTS AND DISCUSSION

The ability of poly(vinylacetylene) to cyclise and form ladder structures increases its thermal stability [2]. Thermal treatment of the formed ladder polymer leads to the formation of a polyaromatic carbonised structure [2], which would seem to be favourable for its use as a carbon fibre precursor. The important prerequisite for this

application would be the need to synthesise polymers with processable molecular weights.

Anionic polymerisation of the lithium salt of monovinylacetylene and subsequent reprotonation yielded a processable polymer with a weight average molecular weight of 13,000 and a polydispersity of 2.4. The polymer softened at 90-100°C and could be spun into filaments from the melt.

A TG analysis of the infusibilised polymer under a nitrogen atmosphere showed an overall carbon yield of 35% (38% of the theoretical yield). This low value is comparable with similarly low values in the case of unoxidised PAN homopolymers. This could partially be a result of its relatively low average molecular weight. In addition to this, the formation of imperfect ladder structures due to the atacticity of the polymer and the simultaneous formation of crosslinks could further lower the thermal stability of the material, as in the case of PAN.

An improvement in the carbon yield is obtained by an oxidation stage prior to carbonisation. Oxidation of the infusibilised fibres leads to the introduction of carbonyl and hydroxyl groups in the structure that lead to the dehydrogenation reactions at higher temperatures (above 300°C). This dehydrogenation results in the formation of aromatic structures that increase the thermal stability of the fibres. Oxidation of the fibres for progressively longer periods results in progressively higher carbon yields. Oxidation for exceedingly long periods, however, leads to an excessive amount of carbonyl groups in the structure and a consequent lowering of the overall carbon yield. The TG analysis is shown in figure 1.

CONCLUDING REMARKS

The carbon yield obtained on the carbonisation of a given sample of poly(vinylacetylene) can be improved by a preliminary oxidative treatment of its fibres in air. A higher oxidation temperature and a smaller fibre diameter will reduce the

optimum oxidation period.

We believe that the process for the conversion of these fibres into carbon and graphitic fibres should be similar to the process employed for PAN fibres. The formation of the basic graphitic structure will take place in the low temperature region and the inducement of orientation at this stage would probably be more important than a similar process at higher temperatures. The main advantage of this system would be the absence of nitrogen incorporated into the aromatic structure created after stabilisation.

REFERENCES

- [1] H.D.Verkruijsse & L.Brandsma., *Synth. Comm.*, **20(21)**, 3355 (1990).
- [2] V.N.Salaurov, Y.G.Kryazhev, T.I.Yushmanova, T.I.Vakulskaya & M.G.Voronkov, *Makromol. Chem.*, **175**, 757 (1974).

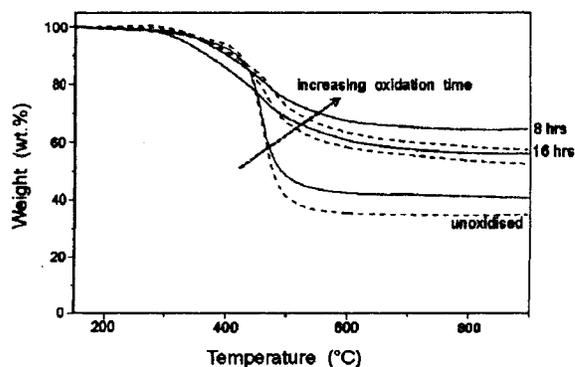


Figure 1: TG analysis of infusibilised poly(vinylacetylene) fibres subjected to different periods of oxidation.