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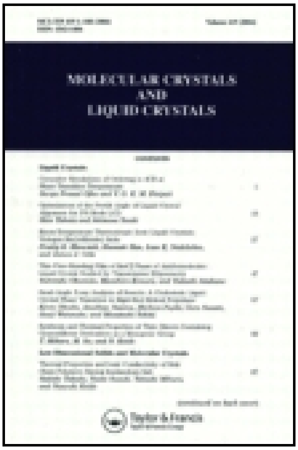

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Transformation, Isomerization and Doping of Polyacetylene Precursor Polymer

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TRANSFORMATION, ISOMERIZATION AND DOPING OF POLYACETYLENE PRECURSOR POLYMER

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Abstract Polyacetylene, produced directly from acetylene is a high surface area aggregate of small particles or fibrils, so that the measurement of transport properties is difficult. We describe studies of polyacetylene produced as a dense, uniform film from a processable precursor and show how we can obtain diffusion coefficients for small species in polyacetylene.

INTRODUCTION

A major problem in the study and application of conducting polymers is that they become progressively infusible and insoluble as they become conducting. This hinders efforts to produce the materials as fibres or films and makes characterisation difficult. Feast et al[1] have described soluble precursor polymers, which can readily be solvent-cast into films or fibres and then converted into polyacetylene by heating. This polyacetylene differs from the product of conventional, direct polymerization of acetylene in that it is amorphous as normally prepared, although crystallinity can be induced by suitable treatments.

The conversion of precursor to polyacetylene involves three stages as revealed by DSC analysis (Fig 1). The initial elimination of aromatic units from the polymer (transformation), evaporation of the volatile product from the polymer and, finally, isomerisation of the initial, largely cis, polyene to the all-trans isomer. By careful, slow, heating the transformation can be taken to completion without allowing isomerisation, which can then be studied in isolation.

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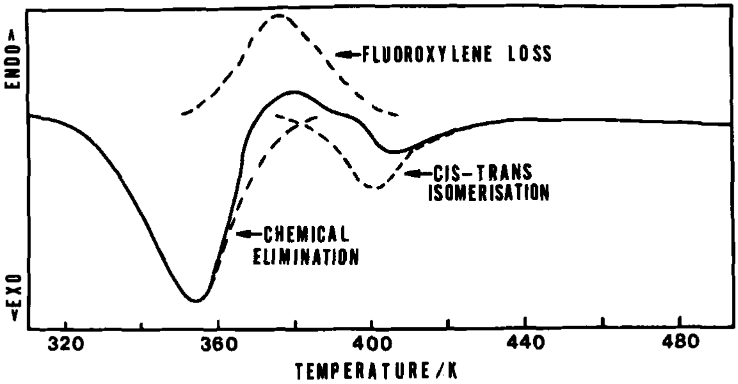

FIGURE 1 DSC trace for heating of a typical precursor polymer. The three separate processes into which the trace can be resolved are indicated.

In this paper we describe studies on the prototypical polymer of this type, poly(5,6-bis(trifluoromethyl)-bicyclo(2,2,2)octa-5,7-diene-2,3-diyl)-1,2-ethenediyl), which converts to polyacetylene by elimination of perfluoromethylxylene. We have studied its conversion into polyacetylene, the isomerisation of the product to amorphous trans-polyacetylene and the diffusion of dopants within the material.

THE TRANSFORMATION REACTION

The precursor polymer was prepared by the method of Feast et al[1]. The number-average molecular weight of the polymer, estimated by GPC, corresponded to a polyene chain of about 7500 acetylene units. The transformation reaction was followed by observing the weight loss of films heated in vacuo and thin enough (<5μm) that xylene diffusion was not rate limiting. The weight change was measured either by using a quartz spring balance or by observing the change in the resonance frequency of a quartz oscillator crystal coated with a thin polymer film. We find that the reaction has first order kinetics up to at least 90% conversion, with an activation energy of 99kJ/mol. This is in good agreement with kinetic analysis of the DSC results, which give first order kinetics and an activation energy of 95kJ/mol.

After transformation in thin films the residual fluoroxylene content of the polymer could be reduced to less than 1.5%, as determined by ir measurements of the very intense C-F stretching vibrations at around 1300cm^{-1}.

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THE ISOMERIZATION REACTION

The polymerisation catalyst which we use gives a precursor polymer which has equal numbers of cis and trans double bonds. The elimination reaction is always cis, so that transformation at temperatures low enough to prevent isomerisation should give a polyene with 75% cis and 25% trans double bonds. This has been confirmed by ir spectroscopy, using the trans vibration at 1000cm^{-1} and the cis vibration at 740cm^{-1} and a relative molar absorption coefficient of 1.5. On warming, isomerisation to all trans polyacetylene occurs and can be monitored by ir. We find that at temperatures of 50 and 60°C the reaction is first-order down to at least 2% cis content. At higher temperatures the reaction becomes second order at least down to a residual cis content of 25%, with an activation energy of 125kJ/mol. Analysis of the DSC data similarly gave a reaction order of 1.8, with an activation energy of 140kJ/mol and a heat of reaction of 10kJ/(mol cis). After long isomerisation times there were no detectable cis units in the polymer. For these measurements air was rigorously excluded from the ir cell. In the presence of 50torr of dry air the low temperature rates were significantly higher, as shown in Figure 2, which also compares our results with those of Shirakawa et al[2] and of Gibson et al[3], for conventional polyacetylene.

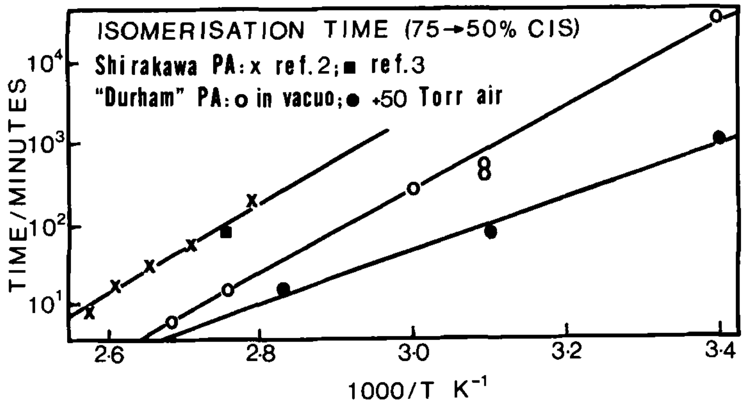

FIGURE 2 Comparison of times for isomerisation from 75 to 50% cis content for polyacetylenes of different origin.

Since Gibson et al found complex reaction kinetics and Shirakawa et al found a temperature-dependent activation energy, we have directly compared times for conversion from 75% to 50% cis. We find that polymer formed by the precursor route isomerises about 6 times faster than conventional material. This may be due to the amorphous nature of the polymer produced from precursor or to a higher concentration of chain defects.

DIFFUSION PROCESSES

Many transport measurements made on conventional polyacetylene are dubious because of the complex morphology. In contrast precursor polyacetylene yields uniformly dense materials whose properties can easily be determined. We have made electrochemical measurements of the diffusion of dopant ions using the galvanostatic pulse method of Winn et al[4].

The cell consisted of a polyacetylene electrode, coated on a nickel mesh and immersed in a solution of lithium perchlorate in propylene carbonate. The counter electrode was lithium. Initially the polymer was doped to about 0.4% Li^+ and allowed to equilibrate for 48 hr. A small pulse of current was then applied to enhance or deplete the concentration of Li^+ at the polymer surface. The EMF of the electrode, measured against a reference electrode, was then monitored as diffusion caused equilibration of the surface with the bulk polymer. We were then able to determine the diffusion coefficient for Li^+ from the slope of the linear plots of EMF against $(time)^{1/2}$. Similarly the diffusion coefficient of perchlorate ions was determined using a cell with a platinum anode and polyacetylene cathode. We obtain diffusion coefficients of $(2.5 \pm 0.5)\times10^{-13}$ cm^2s^{-1} and $(1.3 \pm 0.1)\times10^{-14}cm^2s^{-1}$ for Li^+ and ClO_4^- respectively. These results contrast with estimates by other workers of the order of $10^{-17}cm^2s^{-1}$ for diffusion into fibrillar polyacetylene.

REFERENCES

1. J. H. Edwards, W. J. Feast and D. C. Bott, Polymer 25, 395 (1984).
2. T. Ito, H. Shirakawa and S. Ikeda, J. Polymer Sci. Chem. 13, 1943 (1975).
3. H. W. Gibson, W. M. Prest Jr., R. A. Mosher, S. Kaplan and R. J. Weagley, Polymer Preprints 24(2), 153 (1983).
4. D. A. Winn, J. M. Shemilt and B. C. H. Steele, Mater, Res. Bull., 11, 559 (1976).

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