Preparation of poly(p-phenylene vinylene) deuterium labelled in the vinylene positions

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The preparation of poly(p-phenylene vinylene) specifically labelled at the vinylene positions is herein described. The extent of deuteration is estimated by i.r. spectroscopy, and the mechanism of hydrogen/deuterium exchange during the polymerization process is discussed.

(Keywords: poly(*p*-phenylene vinylene); synthesis; deuterium labelling; conducting polymers)

Introduction

The molecular structure and orientation of poly(p-phenylene vinylene) (PPV) in the solid state have been studied by X-ray and electron diffraction[1,2], i.r. spectroscopy[3,4] and recently by solid state n.m.r. techniques[5,6]. Solid state deuterium quadrupole echo n.m.r. is an effective method for studying molecular motion and orientation in highly conjugated, conducting polymers[7,8] such as poly(p-phenylene)[9], polyaniline[10] and PPV[11]. ^2H n.m.r. has been used to study the chain orientation distribution and the degree of crystallinity in stretched PPV films and to characterize PPV ring flip and chain motions[5,11]. Specifically labelled deuterated samples are required in these structural studies. The experiments mentioned above have been performed using aryl ring deuterated samples prepared from perdeuterated starting materials[5,9]. However, the preparation of perdeuterated or ring deuterated polymer samples depends on the availability of the corresponding deuterated starting materials, which limits the applicability of this type of investigation for other PPV derivatives. Vinylene deuterated PPV provides a simple alternative for these n.m.r. spectral analyses, and, furthermore, the preparation of this material requires only protonated starting materials. A procedure for the preparation of the vinylene deuterium substituted PPV derivative is reported here together with a characterization of the H/D exchange during the preparation of PPV precursor polymer. This procedure can readily be used for vinylene deuteration of other PPV derivatives. In addition to ^2H n.m.r. studies, both phenylene and vinylene deuterated PPVs enable complementary i.r. spectral studies to be made, and some i.r. data are reported here.

Experimental

Materials. α,α'-Dichloro-p-xylene and tetrahydrothiophene were purchased from Aldrich. p-Xylene bis(tetrahydrothiophenium chloride) was synthesized as previously described[12]. Deuterium chloride (D, 99.5%, 35% in D_2O) and sodium deuteroxide (D, 99.8%, 40% in D_2O) were obtained from Cambridge Isotope Laboratories. Deuterium oxide (D, 100.0%, Aldrich) and hexane (h.p.l.c. grade, Fisher) were used as received.

Synthesis of the polyelectrolyte precursor polymer. p-Xylene bis(tetrahydrothiophenium chloride) (10.6 g, 30.0 mmol) was dissolved in 100 ml of D_2O and then mixed by magnetic stirring with 100 ml of hexane in a 500 ml, one-neck round bottom flask. The suspension was purged with argon gas for 20 min and cooled to 0°C in an ice bath. To the above suspension was added 60 ml of 0.5 N NaOD in D_2O (argon purged, 0–5°C) under an inert atmosphere. White gels formed shortly after the base addition, and the two phases separated. The hexane was decanted and the system was neutralized with deuterium chloride (0.5 N in D_2O). The gels were redissolved by adding 300 ml of deionized distilled water and stirring the mixture vigorously. The resulting solution of partially deuterated precursor polymer was then dialysed against deionized distilled water for 4 days with Spectrapore membranes (Fisher, M_W cut-off 6000–8000).

Polymer preparation. The polyelectrolyte solution prepared as above was concentrated under reduced pressure at room temperature. Thin films for i.r. and n.m.r. measurements were prepared by solution casting onto a flat poly(methyl methacrylate) surface using a viscous solution (0.5–1% w/v) and the solvent removed by evaporation under a nitrogen stream or *in vacuo*. The resulting vinylene deuterium substituted PPV films were oriented at 120°C by methods described elsewhere[2,4,5].

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Table 1 Vinylene deuterium content derived from i.r. absorption intensities

I.r. frequency, v (cm^{-1})	Deuteration[a] (%)
1518	62.8
839	67.5
556	60.5

[a] $$\text{Deuteration} = \left[1 - \left(\frac{A^{3025\ cm^{-1}}_{\text{deuterated PPV}}}{A^{v}_{\text{deuterated PPV}}}\right) \Big/ \left(\frac{A^{3025\ cm^{-1}}_{\text{PPV}}}{A^{v}_{\text{PPV}}}\right)\right] \times 100$$

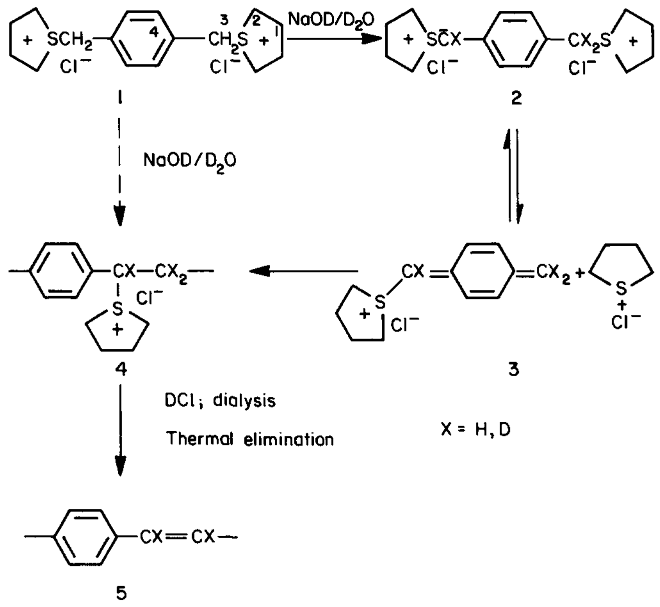

Figure 1 Synthetic scheme for the preparation of vinylene deuterium labelled poly(*p*-phenylene vinylene) (**1** → **4** → **5**) and possible polymerization pathway (**1** → **2** → **3** → **4** → **5**)

Final conversion of the polyelectrolyte into fully conjugated PPV was carried out by heating the polymer films under vacuum at 300°C for 5 h.

I.r. measurements. I.r. spectra were obtained with an IBM model 32 Fourier transform i.r. spectrometer. All spectra were collected on free-standing films with 2 cm^{-1} resolution and over 100 scan counts. Values for percentage deuteration in *Table 1* were determined from the expression given in the footnote to *Table 1*. The variable vinylene CH stretch at 3025 cm^{-1} was normalized relative to each of the constant peaks at 1518, 839 and 556 cm^{-1} for protonated and deuterated PPV, respectively.

Results and discussion

Proton–deuteron exchange. Figure 1 illustrates the synthetic route for the preparation of PPV labelled at the vinylene positions. The procedure is straightforward, convenient in practice, and ultimately provides PPV films selectively labelled at the vinylene positions. The yield of polymer is typically the same as that obtained for protonated material. The percentage deuteration can vary and depends principally upon the length of exposure of the precursor polymer to H_2O. A 64% deuteration was obtained for the material reported here. In particular, the polyelectrolyte benzylic protons that yield deuteration at the vinylene positions remain moderately labile and back-exchange over a period of days during the dialysis step.

It can be shown by ^1H n.m.r. analysis that the tetrahydrothiophenium monomer does not undergo rapid H/D exchange at a neutral pH, and rapid exchange occurs first during the polymerization reaction, after the addition of NaOD. *Figure 2* shows a ^1H n.m.r. spectrum of the monomer salt after several hours in D_2O solution. Peak 3 at 4.4 ppm results from the benzylic protons and has the full integral intensity corresponding to four protons. The 64% deuterium incorporation could have potentially resulted from competition between polymerization and exchange during the polymerization reaction. However, base-catalysed exchange of benzylic sulphonium salts through the ylide mechanism[14] is known to be of the order of milliseconds, and full exchange can readily occur[13] during the (~1 h) time-scale of the reaction. Simpson *et al.*[5] have also reported >95% vinylene protonation for the specifically ring-labelled PPV precursor obtained from perdeuterated monomer. Their preparation was similar but employed a precipitation and washing step rather than dialysis. The procedure of Simpson *et al.* was used for vinylene deuteration and led to >95% deuteration. These observations, with the present experiment, suggest that the precursor polymer is labile during the dialysis step, but back-exchanges over a period of days (−36% over 72 h); however, exchange during the polymerization (when D_2O is present) is complete.

Earlier studies of the PPV precursor polymerization mechanism[13] have shown that the base-induced polymerization proceeds through an equilibrium between an ylide (**2**, *Figure 1*) and an active *p*-xylylene structure (**3**), the latter subject to polymerization to provide the electrolyte (**4**). In $CD_3OD/NaOCD_3$ at $< -40°C$, only deuterium replacement of the benzylic protons of monomer salts occurs, as shown by broadening in the ^1H n.m.r. spectrum of this peak and its merger with the HOD peak. At higher temperatures, elimination of dialkyl sulphide occurs, with concomitant polymerization. The results of this previous study[13] show that exchange occurs faster than elimination to the *p*-xylylene and its polymerization. While these findings need not strictly apply to reactions in D_2O at 0°C, it seems unreasonable to assume that they do not. Thus, established precedent supports the idea that the major H/D exchange in D_2O occurs prior to the formation of the polyelectrolyte polymer and that slow 'washing-out' of deuterium due to prolonged dialysis is a subsequent reaction.

Retention of vinylene deuterons. The i.r. spectra of PPV and vinylene deuterated PPV in *Figures 3A* and *B*, respectively, show that deuterium is retained during elimination without scrambling. The substitution for hydrogen by deuterium can also provide valuable information about specific i.r. vibration modes and assists in i.r. spectral assignments[14]. The vibration band at 2227 cm^{-1} in *Figure 3B* is assigned to the vinylene C/D stretch mode corresponding to the C-H stretch band observed at 3025 cm^{-1} in PPV (*Figure 3A*) and with significantly reduced intensity in *Figure 3B*. The vinylene C-H out-of-plane bending mode at 965 cm^{-1} is shifted

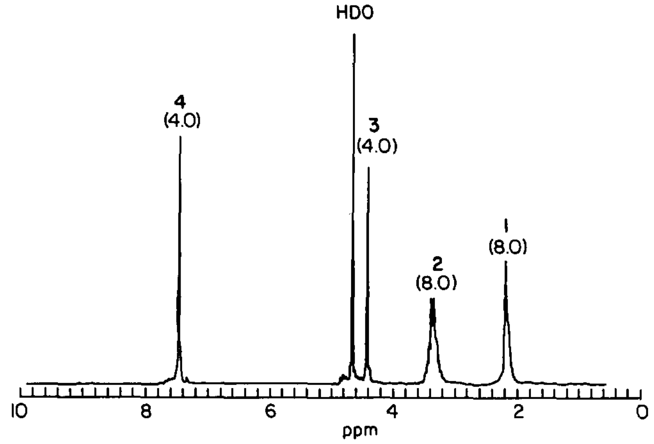

Figure 2 ^1H n.m.r. spectrum of *p*-xylene bis(tetrahydrothiophenium chloride) in D_2O. Peak labels correspond to numbers 1–4 in *Figure 1*(1). The integral (number of protons) is given in parentheses above each peak

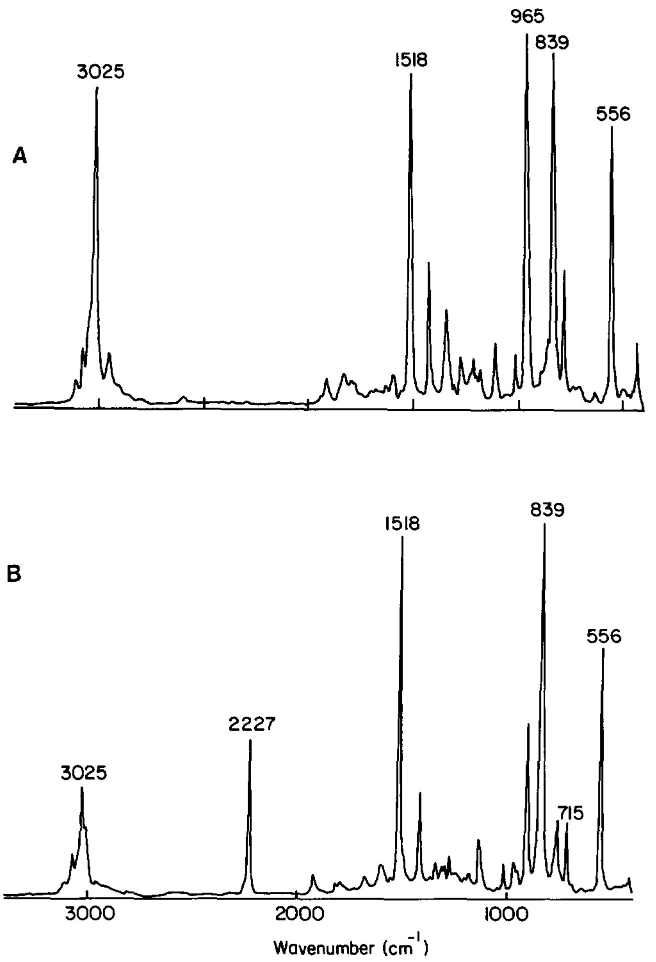

Figure 3 I.r. spectra of (A) poly(*p*-phenylene vinylene) and (B) vinylene deuterated poly(*p*-phenylene vinylene). Peaks of interest are labelled (cm^{-1})

to 715 cm^{-1} upon deuterium substitution. However, the ring-related vibration bands at 1518, 839 and 556 cm^{-1} remain strong and unshifted. Based on the relative intensities of the vinylene C-H stretch mode (3025 cm^{-1}) with respect to these constant ring modes, the extent of deuterium substitution in the converted conjugated PPV was determined and the results are listed in *Table 1*. The same absorption coefficient is assumed for each band in both PPV and vinylene deuterated PPV.

The extent of deuteration of vinylene units is also estimated by ^{13}C cross-polarization/magic angle spinning n.m.r. with interrupted decoupling[5,15] and the value derived by n.m.r. (60 ± 5%) is in agreement with the i.r. data. Although the vinylene units are not completely deuterated, full deuteration is not needed for ^2H n.m.r. studies because of the sensitivity and selectivity of this method[7,8]. The molecular motion and orientation are assessed by analysing the deuterium line shape and the orientation dependence of the resonance frequencies of the individual vinylene C-D vectors with respect to the external magnetic field. These results will be compared with the corresponding studies performed on PPV, specifically deuterated on the phenylene ring, that is, poly(*p*-2,3,5,6-tetradeutero-phenylene vinylene), in a separate report.

In summary, we have described a convenient procedure for the preparation of PPV deuterated in vinylene positions that can readily be applied to other PPV derivatives. The deuteration experiments provide insight into the H/D exchange during polymerization.

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