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A multitechnique investigation of sodium-doped poly(*p*-phenylene vinylene)

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Dopant uptake in sodium-doped poly(*p*-phenylene vinylene) (PPV) has been measured, and e.s.r. spectroscopy has been used to follow the changes in unpaired spin concentration as the doping reaction proceeds. ^{2}H n.m.r. line shapes of sodium-doped, ring-deuterated PPV (PPV-d_4) have also been studied to observe the effects of doping. They contain two distinct components, one of which is attributed to hydride formation. The overall pattern is insensitive to temperature changes.

(Keywords: poly(*p*-phenylene vinylene); n.m.r./e.s.r. spectroscopy; doping)

INTRODUCTION

Fully conjugated polymers, such as poly(*p*-phenylene vinylene) (PPV) (*Figure 1a*), exhibit a variety of specialized physical properties such as electrical conductivity[1–3], non-linear optical activity[4–6], and electroluminescence[7,8]. One important aspect of sample processing involves the removal or addition of electrons to the polymer chains (doping), which in some ways is analogous to the treatment of silicon to generate semiconductors. Removal and addition of electrons can yield information on both the electronic structure and the chemical reactivity of these systems.

A variety of analytical and spectroscopic techniques has been used to study PPV and analogous systems with the goal of understanding the fundamental chemistry and physics of fully conjugated organic systems in the solid state; commonly used techniques include i.r. spectroscopy[9–11], X-ray diffraction[12,13], electron diffraction[14,15], electron microscopy[16], optical spectroscopy[17–19], electrochemical methods[20–22], and e.s.r.[23,24] and n.m.r. spectroscopy[25–28]. Furthermore, a number of chemical reagents, including the alkali metals[29–36], have been used to dope PPV and other polymers. This contribution focuses on the chemical and physical changes brought about in the PPV crystal lattice upon doping with sodium vapour. By combining the data obtained from various methods, we have obtained a more complete picture of the n-doping process of PPV. Thus elemental analysis has revealed the stoichiometry of the sodium doping reaction of PPV; e.s.r. spectroscopy was used to follow the concentration of unpaired spins in the sample at various levels of sodium uptake, whereas deuterium n.m.r. of a ring-deuterated PPV (PPV-d_4) (see *Figure 1b*) was used to examine the doping-induced changes in the electronic environment of the PPV chains and also gave information on the chemistry of the doping reaction. The results of these experiments are correlated and compared with those of Chen *et al.*[29], who used X-ray diffraction to study the sodium doping of PPV.

EXPERIMENTAL

Sample preparation

Protonated PPV and ring-deuterated PPV (PPV-d_4) (*Figure 1b*) were synthesized by a standard precursor polymer route[26,37–42]. Free-standing films of PPV and PPV-d_4, typically 30 μm thick, were sealed in an evacuated glass ampoule with a small amount of sodium metal and placed in an oven at 220°C for 24–168 h. After the glass ampoules containing the doped PPV film and residual sodium metal were removed from the oven, they were introduced into a glove box under an argon atmosphere and transferred into either 5-mm n.m.r. tubes (Wilmad 506-pp), sealed quartz e.s.r. tubes (Suprasil), or airtight sample vials for elemental analysis. As noted by Chen *et al.*[29], the times required for saturation doping (or the attainment of any given level of sodium uptake) varied as a function of several experimental parameters, including the doping vessel geometry and that of the samples themselves.

Figure 2 shows the arrangement for a typical sodium doping protocol. In general, there were three stages of doping that could be visually observed. At short doping times (< 12 h), the portions of the film nearest the sodium turned a deep blue in colour. As the heating continued and the doping reaction proceeded, the bluish colour extended in a direction away from the sodium source and was replaced by another phase near to the metal. The latter had a golden metallic lustre and, of the three

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visually distinct phases that were obtained, was the easiest to prepare quantitatively under the doping conditions employed. At very long doping times (~7 days), regions of the PPV sample nearest to the sodium metal assumed a grey-black colour with a rough appearance, in marked contrast to the smooth, metallic appearance of the 'golden' phase.

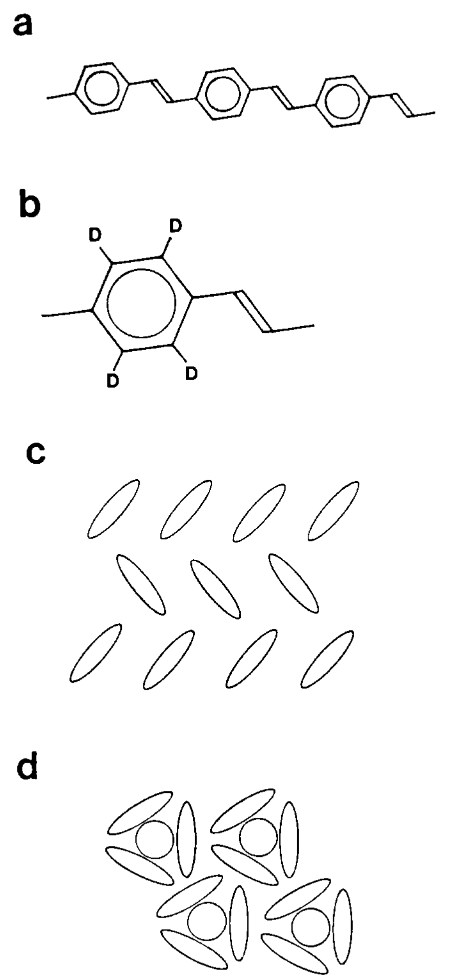

Figure 1 (a) Structure of the PPV repeat unit; (b) locations of the deuterons in PPV-d_4; (c) herringbone packing arrangement of the chains when viewed end-on and; (d) hexagonal packing arrangement of chains viewed from the same perspective, where the circles denote the sodium channels

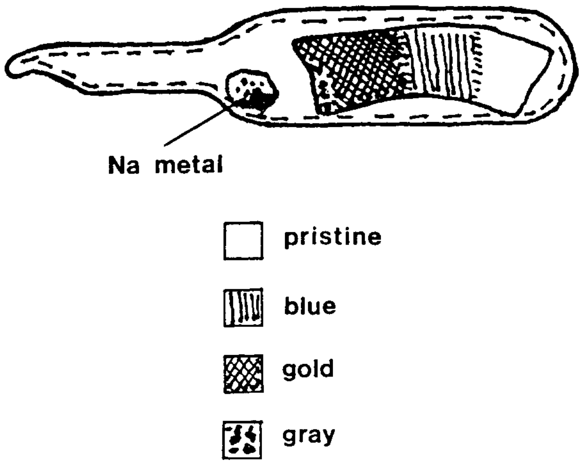

Figure 2 A schematic representation of the heterogeneity of the doping reaction that results under the conditions employed (see text for details)

Table 1 Elemental analysis results for sodium-doped PPV

Phase	Carbon (wt%)	Sodium (wt%)	Number of sodium atoms per C_8H_6 repeat unit
Blue	88–92	2–6	0.08–0.22
Gold	76 ± 3	18 ± 1	0.98 ± 0.04
Grey	<73	>22	>1.24

Table 2 E.s.r. results obtained for sodium-doped PPV

		Peak-to-peak width (G)		Repeat units per spin	
Phase	g-Value	25°C	−196°C	25°C	−196°C
Blue	2.0032	5.6	3.6	730	850
Gold	2.0035	7.0	3.9	400	270

Elemental analyses for sodium, hydrogen, and carbon content were carried out on samples of the three phases (i.e. blue, gold, and grey) at the University of Massachusetts Microanalytical Laboratory (see *Table 1*).

Electron spin resonance (e.s.r.) spectra of samples of both the blue and the gold phase were obtained at −196 and 25°C. Typical sample masses were 1.50 mg, with the samples weighed on a Cahn microbalance. The e.s.r. spectra were collected on a Bruker ESP-300 e.s.r. spectrometer. Doubly-integrated e.s.r. spin counts were calibrated by using a standardized sample of 1,1-diphenyl-2-picrylhydrazyl (DPPH) dispersed in a poly(methyl methacrylate) (PMMA) film according to a previously published procedure[43]. Low-temperature e.s.r. spectra were obtained by placing the e.s.r. tube containing the sample in a liquid-nitrogen-containing Suprasil finger dewar inside the resonance cavity. The g-values of the resonances and peak-to-peak widths of the derivative line shapes were measured by standard techniques, and the results obtained are given in *Table 2*.

Deuterium n.m.r. line shapes were obtained on a Bruker MSL-300 n.m.r. spectrometer with the standard quadrupole echo pulse sequence[44]. *Figure 3* shows the line shapes that were obtained for various samples. Standard variable-temperature equipment was used to vary the sample temperatures from −125 to 175°C, and these lines shapes are shown in *Figure 4*. A special probe insert (to mount on the Bruker High Power probe) was constructed to allow the acquisition of ^2H n.m.r. line shapes for samples cooled to −196°C. *Figure 5a* shows the insert configuration that allowed attainment of this low temperature, and *Figure 5b* shows the line shape that was obtained under these conditions.

RESULTS AND DISCUSSION

Figure 1a shows several repeat units of the PPV chain. It should be noted that PPV adopts an all-*trans* configuration, with the *trans*-vinylene groups aligned in a predominantly parallel (*transoid*) configuration[9,11,15,45]. In the crystalline unit cell[14,15], the PPV chains are aligned parallel to each other, and, viewed end-on, the chains pack in a herringbone fashion. Chen *et al.*[29] have shown that sodium doping of PPV induces a structural change in the unit cell. In particular, in the unit cell of sodium-doped PPV, three PPV chains surround a column of sodium ions, and these structures are, in turn,

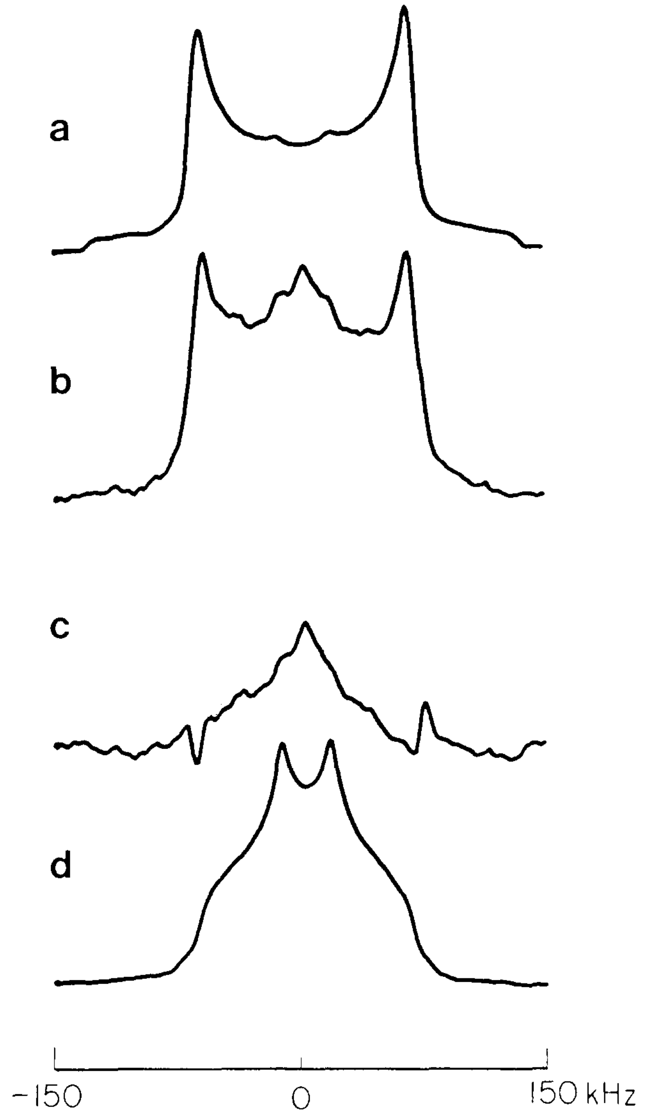

Figure 3 Deuterium n.m.r. line shapes of: (a) pristine PPV-d_4 at 25°C; (b) sodium-doped (gold phase) PPV-d_4; (c) the line shape of (b) minus (a) and; (d) PPV-d_4 at 225°C

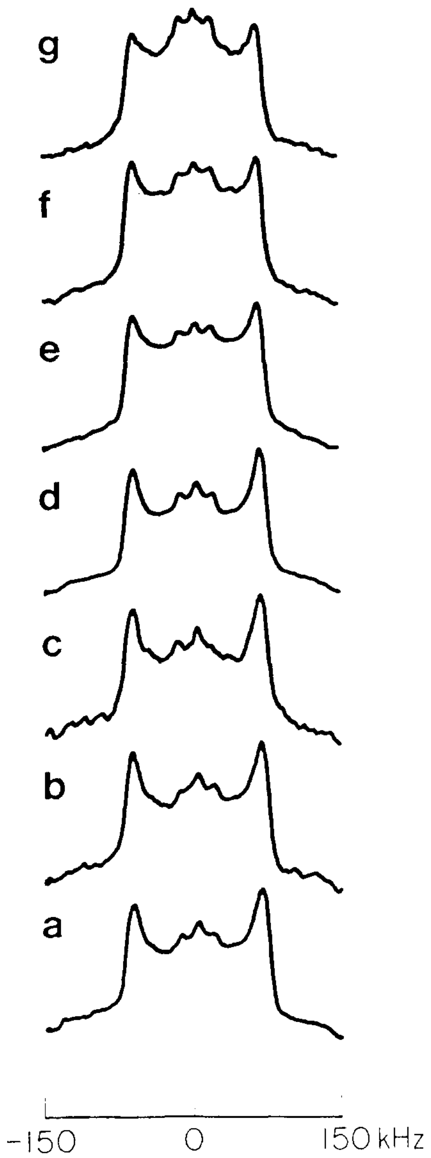

Figure 4 Stack plot of deuterium n.m.r. line shapes obtained from sodium-doped (gold phase) PPV-d_4 at: (a) −125°C; (b) −75°C; (c) −25°C; (d) 25°C; (e) 75°C; (f) 125°C and; (g) 175°C. Note that the line shape is extremely insensitive to temperature changes

packed in a hexagonal lattice. The unit cell of pristine PPV is shown in *Figure 1c*, with the hexagonal phase of sodium-doped PPV given in *Figure 1d*. Another crystal phase is also observed for sodium-doped PPV at higher levels of dopant uptake (> 55 mol% of sodium ions per repeat unit)[29]. The unit cell for this structure is similar to the hexagonal phase of sodium-doped PPV, except that the lateral spacings are larger and the length of the repeat unit (along the crystallographic *c*-axis) is reduced, an arrangement suggesting that the PPV repeat unit is folded or distorted in some manner and is no longer planar. Chen *et al.*[29] have suggested that this distortion is caused by sodium ions that occupy sites outside the sodium channels.

Visual observations on the doping reaction

When PPV is sodium doped, the reaction proceeds in a heterogeneous manner. As already noted, the regions of the film closest to the sodium are observed to dope most rapidly, and those regions of the film that are farthest away dope the slowest. Chen *et al.*[29] have also noted that the kinetics of doping exhibit a strong dependence on the doping vessel geometry. As the reaction proceeds, the PPV film changes in colour from a pristine yellow-orange to dark blue, and then to a metallic gold. Over very long doping times, portions of the sample take on a mottled, grey-black colour with what appears to be a granular surface texture. We have chosen to name these three doping states as the blue, the gold, and the grey phases, respectively.

The blue phase has also been observed by Chen *et al.*[29] at very short doping times. The ^2H n.m.r. quadrupole echo n.m.r. line shape (not shown) obtained from a sample of blue-phase sodium-doped PPV-d_4 was virtually identical to the line shape obtained from pristine (undoped) PPV-d_4. Chen *et al.*[29] have suggested that this phase is due to the incorporation of a very limited amount of sodium ions into the PPV structure, i.e. an amount which was insufficient to convert the bulk of the PPV from the pristine PPV unit cell to the hexagonal-phase unit cell. These authors have determined, by using X-ray diffraction, that the transformation of the unit cell of PPV from the pristine PPV unit cell to the hexagonal-phase

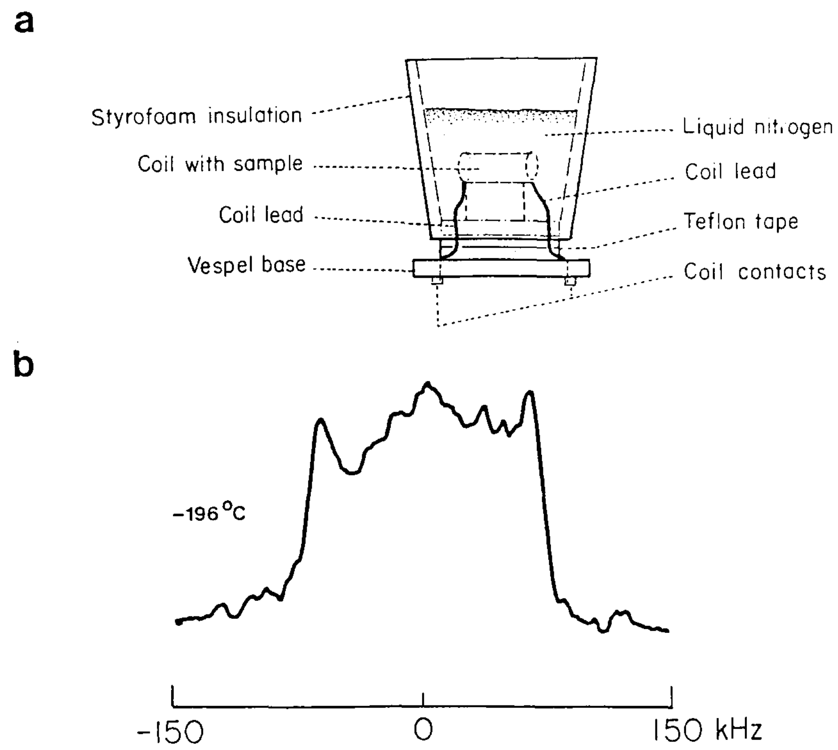

Figure 5 (a) Diagram of the probe insert for acquiring deuterium n.m.r. line shapes at −196°C and; (b) deuterium n.m.r. line shape of sodium-doped (gold phase) PPV-d_4 obtained at −196°C

unit cell does not proceed continuously. At a certain threshold level of sodium uptake, the PPV lattice undergoes a crystal–crystal phase transition. Masse *et al.*[12] have also observed analogous behaviour for various p-doped PPVs. The blue phase is therefore assumed to be PPV that has incorporated only a limited amount of dopant, i.e. a quantity insufficient to bring about the transformation of the unit cell.

With the experimental procedure described above, it was difficult to obtain a sample that is uniformly doped to the blue phase. Under strong illumination, a typical sample of the blue-phase films reveals regions of undoped PPV, which in transmission appear as translucent areas in the middle of what appears to be pure blue-phase material. The difficulty associated with obtaining homogeneous samples of the blue phase suggests that this phase may be thermodynamically unstable with respect to the gold phase, which corresponds to higher levels of sodium uptake. Thus, before a given sample of PPV can be entirely converted into the blue phase, some portions of the sample dope more extensively and form the gold phase. We speculate that the blue phase is produced by the diffusion of sodium into regions of the PPV lattice that are more disordered, and hence more accessible to the dopant molecules.

An observation of Chen *et al.*[29] supports this premise. They show that the PPV in areas that are left undoped as the doping reaction proceeds has slightly smaller lattice constants: X-ray diffraction peaks corresponding to pristine PPV shift to slightly larger angles as the doping reaction proceeds, a result indicating that those crystalline regions left undoped are more dense than those that first undergo the doping process. Moreover, a film of blue-phase material possesses mechanical properties qualitatively similar to those of pristine PPV, a result which also supports the notion that the blue phase is very lightly doped PPV.

In contrast, the gold-phase material is extremely brittle. A pristine PPV film converted into the gold phase has a very highly reflective surface, and a 30-μm thick film of the gold phase is completely opaque. The final, grey, phase of sodium-doped PPV also has very poor mechanical properties. Once a region of the PPV film has reached this latter state, its surface will no longer be specularly reflective and its texture will appear to be rough. It is possible that the grey phase is due to the aggregation of small regions of sodium metal on the film surface, or that the rough appearance of the film surface is caused by a complete breakdown of the PPV morphology. Chen *et al.*[29] have suggested that at the highest levels of sodium uptake, sodium ions no longer confine themselves to the channels shown in *Figure 1d* but in addition occupy interstitial sites, thus distorting the PPV chains from their planar configurations. This conclusion is based on the observation that the characteristic dimension of the PPV repeat unit is reduced from 0.662 to 0.654 nm as the dopant uptake increases from the range of 52–62% to some greater, unspecified value.

At the greater levels of sodium uptake corresponding to the production of a saturation-phase PPV, X-ray diffraction cannot specifically locate the sodium ions in the lattice[29]. This failure indicates that X-ray diffraction alone is not ideally suited to following the incorporation of sodium into the structure of PPV.

Elemental analysis of the three phases

The ratio of carbon to sodium in the three phases has been determined by elemental analysis (see *Table 1*). The uncertainties in the compositions of the blue and the grey phases of sodium-doped PPV are much larger than the uncertainty for the gold-phase material, because these former phases are difficult to obtain in their pure forms, as already noted. The sample of blue-phase material that was analysed in the present investigation had small regions of pristine and gold-phase material present. The grey-phase material also had regions of the gold phase present, a result indicating that the sodium content could in fact be higher than that reported. Column 4 of *Table 1* shows the nominal number of sodium atoms per C_8H_6 repeat unit.

The elemental analyses obtained for the gold phase of sodium-doped PPV clearly show that the doping reaction occurs with a strict 1:1 stoichiometry. We believe that this is the first report of sodium doping of PPV with such a well-defined stoichiometry. However, potassium doping of polyacetylene has also been reported to occur stoichiometrically[46]. The 1:1 level of dopant uptake is significantly higher than any other levels previously reported for PPV-related polymers and stretches the formal definition of this redox process as 'doping'.

The high level of dopant uptake raises the question as to how the sodium ions are able to pack into the PPV lattice. The driving force for the incorporation of sodium into the PPV structure is the redox reaction in which sodium donates an electron to PPV, and the dense packing of the sodium ions into the lattice must give rise to substantial coulombic repulsion. In fact, such repulsion is especially acute in this case because the unit cell of sodium-doped PPV confines the sodium ions to be present in channels lying between three PPV chains. The *c*-axis of the unit cell is 0.662 nm, leaving barely enough room for three sodium ions to fit into one of the columns of the unit cell. The diameter of the sodium ion is 0.195 nm[47], implying that if three sodium ions are packed into each column over the length of the repeat unit, the distance between adjacent positive charges can be only 0.220 nm.

Chen *et al.*[29] have suggested that the increase in the lateral lattice constants (normal to the *c*-axis of the unit cell) that occurs in the progression from the hexagonal phase to the saturation phase could give the sodium ions room to adopt a staggered arrangement in the channels. This arrangement would clearly reduce the coulombic repulsions expected at this high level of sodium uptake.

Electron spin resonance results for the three phases

Another important aspect of the sodium doping process of PPV is the evolution of unpaired spins as a function of the dopant uptake. *Table 2* shows e.s.r. results obtained from samples of the blue phase and the gold phase of sodium-doped PPV-d_4. Column 2 of the table shows the *g*-values that were obtained for the two phases. These values ($g = 2.0032$ and 2.0035) are indicative of carbon-based radicals and are similar to those observed for polyacetylene[48,49]. Columns 3 and 4 of the table show the peak-to-peak widths of the resonances at two temperatures. Interestingly, the widths of the resonances decrease upon cooling of the sample, a result which is not expected for a sample consisting of isolated organic free radicals. This behaviour is more characteristic of metallic systems than of isolated organic ones.

Columns 5 and 6 of *Table 2* show the concentration of spins in the samples at the two temperatures. The concentration is greater at the lower temperature, a result indicating that the unpaired spins are not thermally generated. Furthermore, the concentration of spins is not proportional to the level of sodium incorporated into the samples; the concentration of spins per dopant ion is much higher at low dopant ion concentrations.

This discrepancy cannot be attributed to a concentration of unpaired spins in any pristine PPV present in the blue phase, because PPV is known to possess very low unpaired spin concentrations in its undoped form[23] (a result which has been confirmed by us in control experiments). Instead, the ESR results indicate that at a higher dopant uptake, electrons are donated to the PPV chains and pair to form bipolarons[50,51] or another spinless entity. This general phenomenon has also been observed for p-doped PPV and other conducting polymers. At low doping levels, the concentration of the free spins (polarons[50]) is low enough so that they do not combine to form spinless bipolarons. At higher concentrations, however, the polarons combine, and hence the concentration of spins reaches an upper limit at relatively low dopant uptakes.

Deuterium n.m.r. spectra of the gold phase

Further insight into the doping process was gained by examining the changes brought about in the ^2H n.m.r. line shape of ring-deuterated PPV upon sodium doping. PPV-d_4 is known to undergo thermally activated *p*-phenylene ring flips at ambient and elevated temperatures[26]. At low temperatures, the flip motion of the PPV-d_4 rings will cease on the n.m.r. time-scale and yield a classical Pake doublet ^2H n.m.r. line shape. *Figure 3a* shows the line shape obtained from a sample of pristine PPV-d_4 at a low temperature, for which the quadrupolar splitting is 133 kHz and the asymmetry parameter is 0.03.

The activation energy of the PPV-d_4 ring flip has been previously measured[52], and sulfuric acid doping of PPV-d_4 is observed to increase the ring flip activation energy[53] from 15 to 21 kcal mol^{-1}. There are two possible reasons for this increase. One is that the electronic structure of the PPV backbone may be changed. Specifically, doping of the PPV chain may introduce more double bond character into the single bonds about which the rotation occurs. The other possibility which might account for the increase in the ring flip activation energy could be a steric factor. Sulfuric acid-doped PPV is known to possess a crystal structure different from that of pristine PPV[12]. Together with a new unit cell, the steric constraints imposed on the phenylene rings are likely to be significantly different. Because sodium doping of PPV is known to change the crystal structure of PPV and also to change the electronic structure of the polymer backbone, it was expected that sodium doping might similarly affect the rates of phenylene ring flips as measured by ^2H n.m.r.

Figure 3b shows the line shape obtained from a sample of PPV-d_4 doped to the gold phase. This line shape is composed of at least two distinct components. The broadest component (with a splitting of 131 kHz) can clearly be attributed to static deuterons still present on the *p*-phenylene rings, while the interpretation of the other(s) is (are) less clear. The second component is narrower, with the maxima separated by 64 kHz. There may, in addition, be a third component centred at 0 kHz. *Figure 3c* shows the line shape that results after subtraction of the standard Pake line (*Figure 3a*) from the spectrum shown in *Figure 3b*.

The edges of the difference spectrum shown in *Figure 3c* have an unusual modulation due to the decrease in the coupling constant of the static C–D bonds in the sodium-doped sample. A change in the electronic environment of the polymer chains induced by sodium doping reduces the magnitude of the electrical field gradient and the quadrupolar splitting observed for PPV-d_4 drops from 133 to 131 kHz upon doping.

The difference spectrum shown in *Figure 3c* is qualitatively similar to the spectrum that is obtained from deuterated phenylene rings undergoing 180° flips. *Figure 3d* shows the high-temperature spectrum obtained from PPV-d_4. Note the third (central) component in *Figure 3b* (at 0 kHz), which suggests that there exists an additional phase of deuterated material undergoing rapid, isotropic motion on the n.m.r. time-scale. For H_2SO_4-doped PPV-d_4, it has been shown that deuterons are abstracted from the phenylene rings at elevated temperatures in the form of D_2SO_4 or $HDSO_4$[53]. The deuterated sulfuric acid is mobile at ambient temperatures and contributes a narrow peak to the centre of the ^2H n.m.r. line shape. Thus the possibility that the central component is due to a mobile species must be considered.

To determine whether the second component (64 kHz splitting) of the observed line shape (*Figure 3b*) is attributable to molecular motion, the temperature of the sample was varied. If the component were due to a thermally activated process, it would be expected that temperature variation would change the fraction of rings undergoing this motion on the n.m.r. time-scale with a corresponding change in the observed ^2H n.m.r. line shape.

Figure 4 shows a number of ^2H n.m.r. line shapes that were obtained from a sample of sodium-doped PPV-d_4 at temperatures ranging from -125 to 175°C. We note that the line shapes are very insensitive to changes in temperature, in contrast to that of undoped PPV-d_4[52], or even H_2SO_4-doped PPV-d_4[53]. For undoped PPV-d_4, the line shape varies greatly over the same temperature range. The present behaviour indicates that the narrow component of the sodium-doped PPV-d_4 line shape is due either to a separate mobile phase of deuterated phenylene rings that undergo discrete flips even at very low temperatures, or to deuterons in a different chemical environment, i.e. deuterons that are not bound to carbon atoms. If the energy barrier for ring rotations was close to zero, then the resulting line shape would be further collapsed, with a quadrupolar splitting which was one-eighth of that of the static Pake pattern (the line shape that results from phenylene rings undergoing free rotational diffusion)[54–57].

The possibility that two regions with substantially different molecular mobilities are formed upon sodium doping of PPV-d_4 to the gold phase seems unlikely. Because the coulombic repulsion associated with the products of the doping reaction is expected to be large, a heterogeneous distribution of material phases, with one phase being particularly mobile, also seems remote. Using a specially constructed solid-state ^2H n.m.r. probe insert (*Figure 5a*), we obtained the line shape of sodium-doped PPV-d_4 at -196°C (*Figure 5b*). Although the signal-to-noise ratio is poorer than that for the spectra shown in *Figures 3* and *4*, the results nevertheless show that the narrow component of the sodium-doped PPV-d_4 persists at -196°C. The presence of the narrow component at this temperature strongly suggests that it is not due to a mobile PPV related species.

The alternative to the explanation of the motional collapse of the quadrupolar splitting is that the deuterons are present in some chemical species in the sample other than in a carbon–deuterium bond. A theoretical calculation of the quadrupolar coupling of the gas-phase sodium deuteride molecule[58] is in excellent agreement with the observed quadrupolar splitting of this second component. Abstraction of hydride ions from the phenylene rings of PPV also helps to explain how the positively charged sodium ions are able to pack so tightly into the sodium-doped PPV unit lattice. By incorporating hydride counterions near the sodium ions, the sodium ions are able to pack closely into the unit cell without the energetic penalty associated with assembling like charges in close proximity. Even if the sodium deuteride ion pairs are not exclusively confined to the sodium ion columns, the pairing of these ions helps account for the high density of sodium in the samples.

Other investigations of alkali-doped, fully conjugated polymers have also shown the presence of hydrides[35,36], findings that support our premise. Specifically, polyacetylene doped with potassium has been observed to form hydrides. Abstraction of hydride ions from the PPV chains is also expected to induce large geometrical distortions in the chain. One should note that Chen *et al.*[29] observed both a lateral swelling of the hexagonal phase of the sodium-doped PPV to form the saturation phase, and also a reduction in the length of the repeat unit, suggesting that the chains were no longer planar. It should also be noted that the abstraction of hydride ions from the PPV chains is consistent with the e.s.r. results shown in *Table 2*. The hydride, as with the bipolaron, will go undetected by this technique.

It is important to note that the levels of sodium uptake determined in this study are larger than those imputed from X-ray diffraction[29]. This result indicates that the distribution of sodium ions in the PPV samples is not regular (or commensurate) with respect to the PPV chains in the unit cell. When the sodium doping procedure described in ref. 29 is used, weight uptake measurements[59] indicate that the levels of sodium uptake for comparably doped PPV are in the range 0.7–1.0 sodium atoms per repeat unit, a value substantially larger than that detected with X-ray diffraction (0.55). Whether sodium ions and a sodium hydride pair occupy sites outside of the sodium channels remains to be determined. It is possible that the sodium hydride pairs cause the lateral (i.e. normal to the *c*-axis) swelling of the unit cell or that sodium ions are randomly located in the unit cell. It is clear, however, that at very high dopant uptakes the unit cell of the material is greatly distorted and the PPV chains undergo a chain scission that results in a greatly reduced mechanical stability.

CONCLUSIONS

PPV doped with sodium metal has been observed to form three distinct phases (blue, gold, and grey), which have been characterized by elemental analysis and e.s.r. and deuterium n.m.r. spectroscopy. Elemental analysis indicates that the most uniformly prepared of the three phases (the gold phase) corresponds to PPV with a stoichiometry of one sodium ion per C_8H_6 repeat unit. The evolution of unpaired spins has been examined for the blue and the gold phases at -196 and 25°C and it was shown that the e.s.r. behaviour of these systems is more characteristic of metallic systems than of conventional organic radical systems.

Deuterium n.m.r. spectra of sodium-doped, phenylene-ring deuterated PPV (PPV-d_4) show a line shape that is insensitive to temperature, a result suggesting that the doping process raises the activation of phenylene ring flips so much that the rings can no longer flip on the n.m.r. time-scale, even at 175°C. A central component of the line shape has been assigned to a process in which the abstraction of deuterons from the phenylene rings forms sodium deuteride. Sodium hydride (deuteride) may screen out the extreme coulombic repulsions otherwise associated with the high sodium ion concentration in the samples. The hydride formation also accounts for the severe geometrical distortions observed at high doping levels.

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