A structural investigation of polyvinylpyridine charge transfer complexes by X-ray photoelectron spectroscopy and static secondary ion mass spectrometry

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The charge transfer (CT) interactions and molecular structures involving poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) and various halobenzoquinone acceptors have been studied by X-ray photoelectron spectroscopy (X.p.s.). X.p.s. results suggest that the CT interactions have proceeded beyond the pure formation of molecular CT complexes. The structures of the CT complexes derived from the X.p.s. results are further confirmed by the static secondary ion mass spectrometry (s.i.m.s.) data. The fragmentation patterns of the CT complexes are consistent with the presence of linkages between the pyridinium nitrogens and the various acceptors.

(Keywords: charge transfer; polyvinylpyridine; halobenzoquinone)

Introduction

Electroactive polymers have attracted much attention in recent years. The most commonly studied electroactive polymers include polyacetylene, polyaniline, polypyrrole, polythiophene, poly(phenylene sulfide) and their derivatives and analogues (see, for example, ref. 1). Some non-conjugated electroactive polymers, such as the vinylpyridine[2–4] and vinylcarbazole[5,6] polymers, have also been actively studied. In the investigation of a typical electroactive polymer system, a better understanding of its charge transfer (CT) behaviour is usually sought. Surface analytical techniques, in particular X-ray photoelectron spectroscopy (X.p.s.), have been shown to provide a useful tool for the study of CT interactions in electroactive polymers[7,8]. The applications of secondary ion mass spectroscopy (s.i.m.s.), on the other hand, have been devoted mainly to the study of the intrinsic structures of polymers with saturated backbone[9] and, to a much lesser extent, polymers with conjugated backbone[10,11] and polymeric CT complexes. Our earlier X.p.s. studies on CT complexes involving poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) with various organic acceptors revealed that the CT interactions proceeded further than the pure formation of molecular complexes[12,13]. Thus, taking into account the molecular specificity of s.i.m.s., it should be interesting to study the effects of complex formation on the fragmentation patterns of the two vinylpyridine polymers. In this respect, the s.i.m.s. results also provide further supporting evidence of the molecular structures derived from the X.p.s. technique.

Experimental

The polymer samples consisted of linear P2VP and linear P4VP. Both samples were obtained from Polyscience, Inc., and had average molecular weights of about 40000 and 50000, respectively. The halobenzoquinone acceptors, such as *o*-chloranil, *p*-chloranil, *o*-bromanil and *p*-bromanil, were obtained from Aldrich Chemical Co. All acceptors were recrystallized from appropriate solvents before use. The vinylpyridine polymer films were cast directly onto the X.p.s./s.i.m.s. sample studs from chloroform solutions. The polymer–acceptor complexes were prepared by exposing the polymer films to various acceptor solutions of different concentrations. The X.p.s. measurements were made on a VG Escalab MkII spectrometer with an MgKα X-ray source (1253.6 eV photons). The X-ray source was run at reduced power of 120 W (12 kV and 10 mA). The core level spectra were measured at a take-off angle of 75°. To compensate for surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. Surface chemical compositions were determined from peak area ratios, corrected with appropriate experimentally determined sensitivity factors, and were liable to a $\pm 5\%$ error. The static s.i.m.s. measurements were carried out on a VG Simslab system. The primary ion source was a 4 keV, 0.3 nA Ar^+ beam produced by a differentially pumped VG DP50 duoplasmatron ion gun. The mass-filtered ion beam was incident at 60° to the sample normal and rastered at TV mode over the sample area of about 0.5 cm^2, giving an ion current of about 0.6 nA cm^{-2}. The total data collection time of the positive mass spectra, including instrument tuning time, was less than 360 s. This is equivalent to a total ion dose of about 1.4×10^{12} cm^{-2} for a particular sample and is well within the threshold limit of 10^{13} cm^{-2} for static s.i.m.s.[14]. The normal operating pressure in the analysis chamber was $< 5 \times 10^{-9}$ mbar.

Results and discussion

Recent X.p.s. studies of P2VP– and P4VP–halobenzoquinone CT complexes[12,13] revealed the presence of

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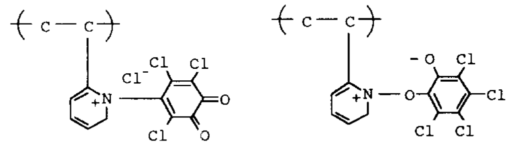
positively charged nitrogen and negatively charged halogen and benzoquinone anion species. The presence of these charged species in the complexes suggests the cleavage of carbon–halogen bonds of the acceptors, resulting in the formation of linkages between the pyridinium nitrogens and the acceptors at the site of the cleavage. The presence of the benzoquinone anions, on the other hand, suggests the linkage of the carbonyl oxygen of the acceptor to the positively charged pyridinium nitrogen. The plausible molecular structures of the complexes, using P2VP–*o*-chloranil complex as an example, are shown below:



The molecular structures of the P4VP CT complexes would be similar to the above structures, except for the position of the pyridinium nitrogen. The X.p.s. results obtained for the present P2VP and P4VP CT complexes agree closely with the published data[12,13]. The extent of CT, as indicated by the proportion of the positively charged pyridinium nitrogens and the amount of anions present in the CT complexes, is limited by the steric hindrance associated with the pyridinium nitrogen at the *ortho* position of P2VP, but enhanced by the presence of sterically less hindered C_4 position of the *o*-halobenzoquinones. Thus, comparatively strong CT interactions are observed in the P4VP–*o*-chloranil and P4VP–*o*-bromanil complexes, resulting in the formation of more than 25% of the halogens anions, as shown in *Table 1*. This result readily indicates that some of the dopant molecules must have reacted with more than one pyridinium nitrogen, either from the same chain or across the chain, resulting in chain distortion or crosslinking, respectively. A crosslinked structure has also been reported for the complexes formed between P4VP, but not P2VP, and copper chloride[4].

The positive s.i.m.s. spectra of pristine P2VP and P4VP are given in *Figures 1a* and *b*, respectively. The spectra are generally similar to those reported in the literature[15]. The positive ion species of 41D corresponds to the major fragment of polyethylene-like[16] backbone and probably a minor contribution from the hydrocarbon portion of the cyclic pendant group of the polymer[17,18]. The relative yields of the characteristic molecular fragments of P2VP and P4VP containing the pyridinium ring with respect to the intensity of the 41D peak would then represent the ease with which the nitrogen-containing pendant groups (78D, 79D, 106D and 130D fragments, see *Figure 1*) dissociate from the polymer chain. The CT interactions with the organic acceptor are expected to result in lower relative ion yields of these species as a consequence of the attachment of the dopant molecules solely to the pyridinium nitrogens of the polymer. The CT interactions should have much less effect on the fragmentation of the polymer backbone and the hydrocarbon portion of the pyridine ring. Thus, the intensity of the 41D fragment represents a valid marker for comparison.

Table 1 presents the relative positive ion yields of the various nitrogen-containing pendant group fragments with respect to the 41D fragment in some of the P2VP and P4VP CT complexes. *Figures 1c* and *d* show the respective mass spectra of the P2VP–*o*-chloranil and P4VP–*o*-bromanil complexes. Although *Figure 1d* shows distinct peaks at 73D and 147D, characteristic of possible contamination by poly(dimethylsiloxane) (PDMS), the much reduced yields of the nitrogen-containing fragments are nonetheless consistent with a higher degree of CT. Furthermore, since PDMS does not contribute significantly to the 41D fragment[19], the intensity of this component is not likely to be affected to an appreciable extent. The positive s.i.m.s. peak at 106D constitutes the major peak of the pristine P2VP and pristine P4VP polymer and consists of the basic structure of the vinylpyridine monomer. The relative positive ion yields of the 78D, 106D and 130D fragments in the P2VP CT complexes and the 79D, 106D and 130D fragments in the P4VP complexes are less than those of the corresponding pristine polymers. Furthermore, for each polymer–halobenzoquinone system, the stronger CT interaction involving the *o*-halobenzoquinone acceptor always results in a higher doping level and a lower ion yield for each fragment containing the pendant group. These results are consistent with the proposed CT complex structure involving linkages between the dopant molecule and the pyridinium nitrogen of the two polymers. The lower positive ion yield in pristine P4VP

Table 1 Relative positive ion yields of the major molecular fragments of P2VP and P4VP CT complexes

Sample	Dopant/monomer ratio[a]	Halogen in the anionic form (%)[b]	Relative positive ion yields			
			78D/41D	79D/41D	106D/41D	130D/41D
P2VP	0.0	0	2.85	–	9.50	2.80
P2VP–*p*-chloranil	0.05[c]	6	2.66	–	6.88	1.61
P2VP–*o*-chloranil	0.30[c]	14	1.74	–	4.58	0.86
P2VP–*p*-bromanil	0.02	22	2.87	–	7.06	1.62
P2VP–*o*-bromanil	0.39	30	1.00	–	4.30	0.65
PV4P	0.0	0	–	0.68	1.54	0.15
P4VP–*p*-chloranil	0.03	26	–	0.14	0.36	0.03
P4VP–*o*-chloranil	0.09	33	–	0.16	0.28	0.03
P4VP–*p*-bromanil	0.02	66	–	0.23	0.70	0.08
P4VP–*o*-bromanil	0.16	60	–	0.19	0.47	0.04

[a] Derived from the sensitivity factors corrected N1s and halogen X.p.s. core level spectral area ratios
[b] Derived from the curve-fitted halogen X.p.s. core level spectra. The rest of the halogens remain covalently bonded to the acceptors
[c] Each polymer film was exposed to the same concentration of the *o*- or *p*-halobenzoquinone solution for approximately the same period

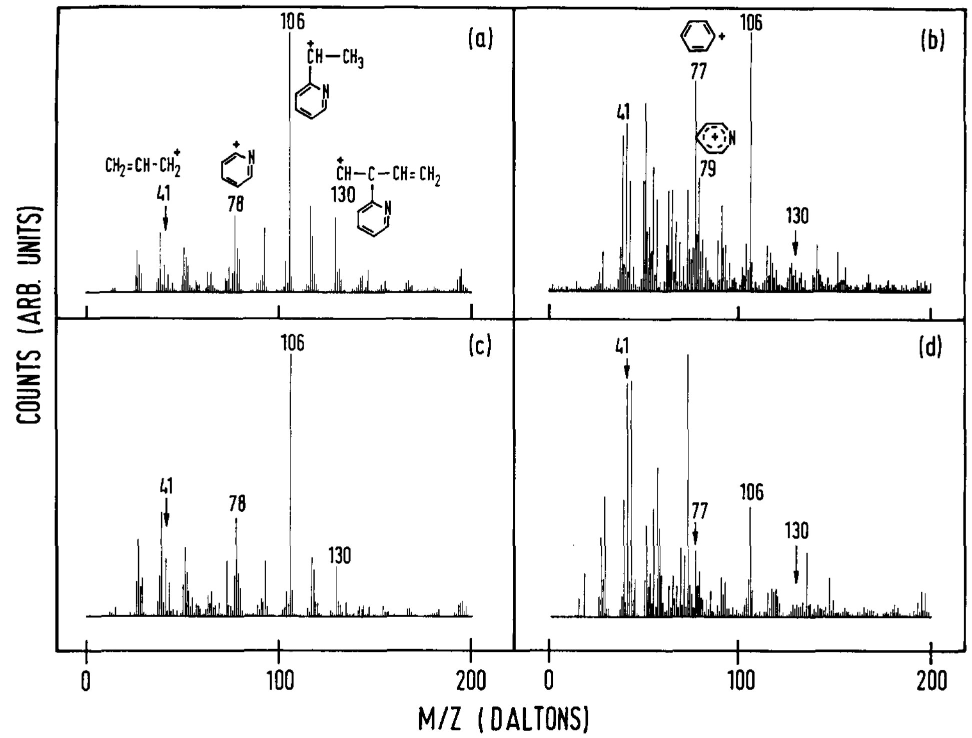


Figure 1 Positive s.i.m.s. spectra of (a) pristine P2VP, (b) pristine P4VP, (c) P2VP–*o*-chloranil and (d) P4VP–*o*-bromanil

is due to the higher intensity of the 41D peak in the P4VP mass spectrum, as shown in *Figure 1b*, suggesting that the linear chain of P4VP has a higher probability of fragmentation. The negative s.i.m.s. spectra of P2VP, P4VP and their CT complexes are not presented as they do not give conclusive evidence on the interaction of the CT complexes.

A direct comparison of the reactivities of P2VP and P4VP complexes is difficult due to the difference in ion yields of the pristine species. Nonetheless, the data in *Table 1* indicate a more drastic decrease in the relative ion yields for the P4VP CT complexes, even though the dopant levels are kept lower than those of their P2VP counterparts. This phenomenon is consistent with the existence of more than 25% of the halogens as the anionic species, and thus the presence of chain crosslinking, in the P4VP complexes studied.

Conclusion

The static s.i.m.s. data provide further evidence in support of the molecular structures of polyvinylpyridine–halobenzoquinone CT complexes derived from the X.p.s. data. The variations in the positive ion yields with respect to the chain fragments give the relative ease with which the nitrogen-containing pendant ring dissociates from the linear chain of the polymer. Thus, for CT interactions which resulted in the formation of linkages between the pyridinium nitrogens and the acceptor molecules, the relative positive ion yields of the pendant group and molecular fragments containing the pendant group are distinctly reduced.

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