The polyvinylphenol–fluoride system: strong hydrogen bonding and polymer derivatization

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Polyvinylphenol forms strong hydrogen bonds with fluoride to an extent dependent on the solvent environment. Remarkable changes in the Fourier transform i.r. spectra and the thermal behaviour of the polymer are observed on formation of strongly hydrogen bonded complexes which can be used as highly nucleophilic forms of the polymer suitable for derivatization.

(Keywords: polyvinylphenol; fluoride; hydrogen bonding)

The properties of a polymer possessing hydrogen bonding groups are known to be influenced by the hydrogen bonds formed between the polymer and other species present in the system, such as the solvent and other hydrogen bonding active polymers. Polyvinylphenol, for example, is expected to be a good hydrogen bond proton donor (electron acceptor) and a rather less good proton acceptor. As with most polymers, however, studies on hydrogen bonding to polyvinylphenol have been largely limited to measurements on polymer–polymer miscibility[1,2].

The fluoride ion is known to be a particularly powerful hydrogen bond proton acceptor (electron donor), and the physical and chemical properties of small molecules strongly hydrogen bonded to the anion are known to be significantly affected by the interaction[3,4]. The nucleophilicity of carboxylic acids, for example, is considerably enhanced by $RCO_2H\cdots F^-$ hydrogen bonding, enabling facile acid derivatization, and more generally hydrogen bond assisted reactions have been widely used for the highly specific derivatization of low molar mass molecules[4]. Little attention has been given to the effects of strong hydrogen bonding on the properties of polymers, although clearly there are many potentially interesting effects that might result from the associated changes in electronic, associative and steric properties. The efficient derivatization of polymers is also a very important subject. We now report for the first time the formation of strong hydrogen bonds between fluoride and polyvinylphenol, and the resulting effects on the properties of that polymer.

Strongly hydrogen bonded complexes of polyvinylphenol and F^- can be prepared by slow addition of a solution of tetrabutylammonium fluoride (TBAF; used as the trihydrate) to a stirred solution of the polymer at room temperature. The amount of TBAF taken up by the polymer and hence the degree of $-O-H\cdots F^-$ hydrogen bonding is solvent dependent and increases in the order acetonitrile < tetrahydrofuran < dimethylformamide. In acetonitrile and tetrahydrofuran, solids precipitate from the solutions and the ^1H n.m.r. spectra (dimethylsulfoxide, DMSO-d_6) of these solids show significantly less TBAF than that corresponding to $1F^-$:1 phenol unit, the residual TBAF remaining in solution. This is consistent with tightly coiled polymer chains (which have a limited number of exposed hydroxyl units) rapidly hydrogen bonding to F^- ions, rendering the subsequent complex insoluble. In dimethylformamide, in which the polymer is relatively uncoiled, no precipitation occurs. After removing the bulk of the solvent under reduced pressure, addition of acetonitrile precipitates a solid complex ($1F^-$:1 phenol unit by ^1H n.m.r.) which was washed with ethoxyethane and dried at room temperature (24 h, 0.01 mmHg).

The Fourier transform i.r. (*FT*i.r.) spectrum of the 1:1 complex reveals the presence of strong hydrogen bonds (*Figure 1*). In particular the broad, single OH stretching band of the pure polymer, which is centred at ~3400 cm^{-1}, is replaced by a complex series of bands in the 3500–1800 cm^{-1} region of the spectrum (centred at ~2500 cm^{-1}). This can be attributed to the formation of strong, easily polarizable $O\cdots H\cdots F^-$ hydrogen bonds which give rise to an extremely broad band that is split by Fermi resonance between stretching and bending modes of the hydrogen bonded unit[5]. A further manifestation of the strong hydrogen bonding is the shift in the C–O stretch from 1230 cm^{-1} in the free polymer to 1260 cm^{-1} in the TBAF complex.

Thermal analysis of the 1:1 polyvinylphenol–TBAF complex is also remarkable in that no weight loss is observed below 200°C, despite this being well above the normal decomposition temperature of TBAF[6]. The exothermic weight loss at 200°C is followed by an

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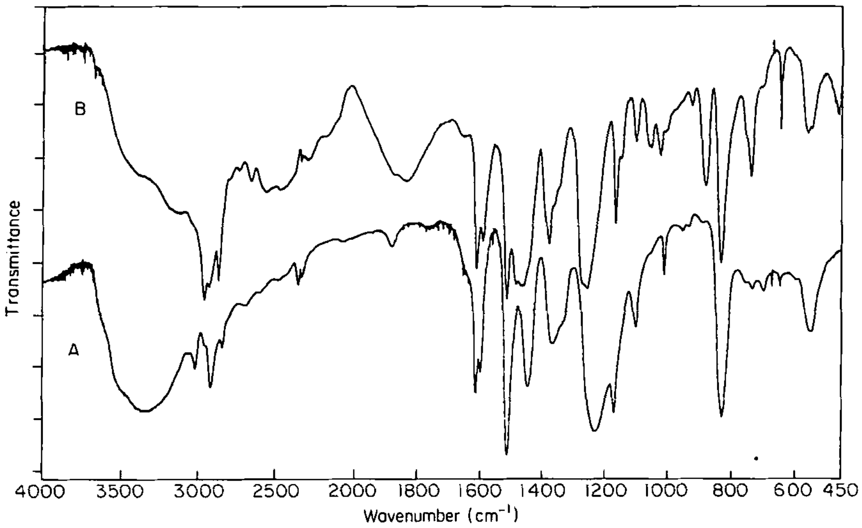

Figure 1 *FT*i.r. spectra (KBr disc) of (A) polyvinylphenol and (B) polyvinylphenol–TBAF (1:1) complex

endothermic weight loss at ~320°C corresponding to polymer decomposition, although this is some 80°C below the decomposition temperature of the pure polymer. This unusual thermal behaviour is the subject of a further publication[7].

In preliminary experiments to test the reactivity of the 1:1 polyvinylphenol–TBAF complex and the use of strong hydrogen bond activation in polymer derivatization, we studied its reactions with iodomethane (to partially cap proton donor sites) and ethanoyl chloride (to introduce new hydrogen bond proton acceptor sites). By stirring a solution of the complex (0.25 g) in DMSO (50 cm^3) with iodomethane (0.4 cm^3) for 2.5 h at room temperature, we were able to achieve ~50% methylation of the polymer (polymer–OH to polymer–OMe). This actually represents quantitative derivatization based on the normal stoichiometry for F-assisted alkylations[4]:

$$\mathrm{ArOH\cdots F^- + RI \rightarrow ArOR + HF + I^-}$$

$$\mathrm{ArOH\cdots F^- + HF \rightarrow ArOH + HF_2^-}$$

No reaction occurs in the absence of the fluoride.

Ethanoyl chloride will react slowly with polyvinylphenol itself but the complex reacts significantly more quickly. This can be readily observed by rapidly stirring a slurry of the complex (0.5 g) in ethanoyl chloride (30 cm^3). A tight polymer ball is quickly formed (indicative of polymer self-association resulting from partial substitution of $-OH$ by $-OCOCH_3$) which then breaks up and fully dissolves within 5 min. In the absence of TBAF, the same effect takes several hours. After 4 h, >80% conversion of polymer–OH to polymer–$OCOCH_3$ has occurred (^{1}H n.m.r.) with the complex whereas <40% conversion is achievable in the absence of TBAF. Interestingly, only small quantities of ethanoyl fluoride were observed in contrast to reactions of $RCO_2H\cdots F^-$ complexes with acid chlorides, which give acid fluorides in competition with carboxylic acid derivatization[4].

The results reported here are consistent with the formation of strong, easily polarizable polymer–OH···F$^-$ hydrogen bonds which cause enhanced phenol nucleophilicity due to high local charge density at the oxygen[8]. We are currently studying the interaction of polyvinylphenol with other sources of F$^-$ and the thermal decomposition of the resulting complexes, along with a more detailed investigation of their synthetic utility.

Acknowledgements

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