

Studies on the nature of the unusually high bulk viscosity of flame retardant prepolymer from cardanol

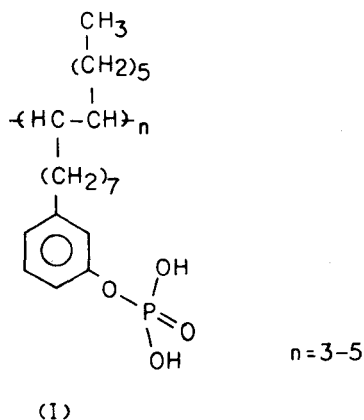
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Phosphorylated prepolymer of cardanol exhibits unusually high bulk viscosity (200,000-250,000 cP) at 29°C. The viscosity undergoes drastic reduction with increase in temperature reaching a very low value of 82 cP at 150°C. The intrinsic viscosity of the oligomers has been studied in a number of solvents differing in polarity. The IR spectra of neat solution shows a broadening and shift in the P=O stretching absorption band at 1250 cm^{-1} with respect to spectra in CCl_4 . These data indicate that presence of hydrogen bonding is probably responsible for the unusually high viscosity exhibited by the system at ambient temperature.

The synthesis of a flame retardant prepolymer from cardanol was reported earlier from our laboratory^{1,2}. The synthesis was carried out by esterification of the hydroxyl group in cardanol with orthophosphoric acid followed by polymerisation through the Π -bonds of the side chain (structure I). The polymerisation was controlled to get a prepolymer containing only oligomers so that the resin could be used as a flame retardant additive as well as a matrix for flame-retardant polymer composite². The phosphorylated prepolymer (PCP) thus obtained, however, showed



very high bulk viscosity which was otherwise unexpected for an oligomeric product. This note reports results of experiments carried out to study the nature of the high viscosity of PCP.

Experimental

Cardanol was used after distillation *in vacuo*. Orthophosphoric acid was a BDH (England) product. The phosphorylated product was washed with water and dried in a flash evaporator. The resin obtained was a light brown liquid, soluble in most of the common organic solvents. It showed a phosphorus content of 7.9%, density 1.2 g/cc and a bulk viscosity of 216,000 cP at ambient temperature (29°C). *m*-Cresol (BDH, England) was used after distillation. The phosphorylation of *m*-cresol was carried out using POCl_3 with AlCl_3 as the catalyst³. The product obtained was hydrolysed using cold water and the *m*-cresol phosphate was collected and purified.

Bulk viscosity measurements were carried out using a Brookfield viscometer, model RVT 230 V, at 29°C and various other temperatures. Intrinsic viscosity was measured using a Ubbelohde viscometer at 40°C. IR spectra were recorded using a Perkin Elmer IR spectrophotometer, model 882.

Results and discussion

Cardanol at 29°C gives a bulk viscosity of 90-100 cP whereas on phosphorylation the viscosity increases to 216,000 cP. Earlier studies² have shown that PCP contains only low molecular weight oligomeric species, the structure of the major component being (I) where $n = 3-5$, so the high bulk viscosity of PCP at ambient temperatures does not originate from chain length alone⁴ but has contributions from secondary forces also such as hydrogen bonding or hydrophobic interactions^{5,6}. In a recent study⁷ on oligomeric poly(propyleneglycol) it was shown that the abnormal behaviour in viscosity of the product was due to entanglements of the transient hydrogen bonded structure. To check this, we studied the behaviour of *m*-cresol, which is a model compound for study with respect to cardanol. *m*-Cresol also showed an increase in viscosity from 25 cP to 490 cP on phosphorylation at 29°C.

It is generally known⁸ that molecules containing phosphate groups exhibit hydrogen bonding which gives rise to changes in properties such as melting point, viscosity, crystallinity, etc. These properties are affected by variation in temperature. Table 1

Table 1—Bulk viscosity of phosphorylated cardanol oligomers at various temperatures

Temp. (°C)	Viscosity (cP × 10 ³)
29	216.00
33	119.68
37	71.20
45	30.56
50	16.51
60	6.08
70	2.66
80	1.87
90	0.56
100	0.30
130	0.12
150	0.082

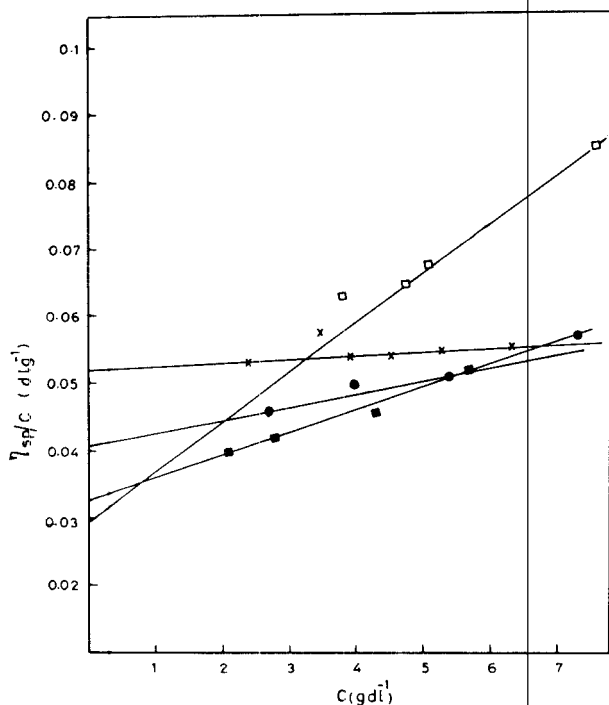
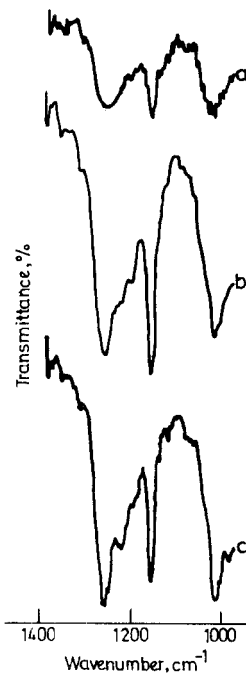


Fig. 1—Plot of reduced viscosity versus concentration for phosphorylated cardanol oligomers in various solvents at 40°C [(□) carbon tetrachloride, (■) xylene, (●) chlorobenzene and (X) ethyl methyl ketone]

shows a drastic decrease in viscosity of PCP as temperature is raised to 150°C. The viscosity dropped from 216,000 cP at 29°C to 82 cP at 150°C.

Figure 1 shows the plots of specific viscosity of PCP versus concentration for different solvents varying in polarity. The intrinsic viscosity of PCP was found to be 0.03, 0.033, 0.041, and 0.052 in carbon tetrachloride, xylene, chlorobenzene and ethyl methyl ketone. Thus, intrinsic viscosity varies with polarity of the


 Fig. 2—Infrared spectra of phosphorylated cardanol oligomers [(a) neat film, (b) one molar solution in CCl₄, (c) 0.3 molar solution in CCl₄]

solvent and has the highest value (0.052 dl gm⁻¹) for the solvent ethyl methyl ketone which has the highest polarity among the solvents selected. The variation of intrinsic viscosity of the prepolymer in solvents differing in their polarities indicates the possibility of interaction between the solvent⁵ and the oligomer involving polar-polar, polar-nonpolar and nonpolar-nonpolar entities resulting in various alignments of the molecules into aggregate groups.

The involvement of hydrogen bonding in the interaction between phosphate groups of the oligomer is revealed by the broadening and shift observed in the IR spectra (Fig. 2) of the oligomer. Figure 2 shows the spectrum of the oligomer alone (neat spectrum), compared to the spectra of the dilute and concentrated solutions of the oligomer in a non-polar solvent such as CCl₄ in which hydrogen bonding is expected to be minimum. The IR bands due to vibrations of P = O, P-O-C etc. groups occur in the region 1250 cm⁻¹ to 1000 cm⁻¹ (ref.9,10). These show definite broadening in the case of the neat spectrum compared to the dilute solution spectrum. The broadening is particularly much more visible in the case of P = O stretching absorption at 1250 cm⁻¹. It can also be seen that there is a shift⁵ by 10 cm⁻¹ in the case of dilute solution. Broadening and shift in the IR bands of P = O group or P-O-C are reported to be a general phenomenon observed with systems that involve hydrogen bonding. It appears from these results that the phosphoryl-

ated oligomer of cardanol exists in aggregates involving hydrogen bonding.

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