

Processable conducting polymers obtained via protonation of polyaniline with phosphoric acid esters

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The protonation of polyemeraldine base (PANI) by diesters of phosphoric acid was studied. Three esters were investigated, namely bis(2-methylpropyl) hydrogen phosphate (DiBHP), bis(2-ethylhexyl) hydrogen phosphate (DiOHP) and its non-branched analogue, bis(n-octyl) hydrogen phosphate (DnOHP). It has been found that DiOHP, in addition to protonation, plasticizes PANI at very low ester contents i.e. for $y \geq 0.25$ in PANI(DiOHP)_y. In PANI(DnOHP), and PANI(DiBHP), the plastification starts at $y = 0.50$ and $y = 0.65$ respectively. It is clear that the long and branched substituents facilitate plastification. PANI protonated with DiOHP is soluble in common organic solvents such as toluene, chloroform, THF etc. The soluble fraction is enriched in DiOHP as compared with the parent protonated polymer. The existence of the anions originating from the ester in the soluble part of the polymer was confirmed by FTi.r. and ³¹P n.m.r. studies of the soluble fraction. Free-standing films with a conductivity of 10 S cm^{-1} can be produced by hot pressing PANI(DiOHP), at temperatures of 80–140°C. At higher temperatures partial degradation of the complex occurs resulting in a decrease of conductivity with a simultaneous increase of Young's modulus and tensile strength. Blends of DiOHP-plasticized PANI and dioctyl phthalate-plasticized PVC, of excellent mechanical properties, can be prepared by hot pressing at 160°C.

(Keywords: polyaniline; processability; protonation)

INTRODUCTION

Polyaniline has been the subject of significant research during the last decade for many reasons, principally that, although less conductive than, for example, doped polyacetylene, it is the most environmentally stable conducting polymer, and it is inexpensive and relatively simple to synthesize.

The main factor that precludes polyaniline-based conducting polymers from a wide range of technological applications has been the lack of processability. In recent years, however, several attempts to improve the processability of polyaniline have been undertaken. In particular, polyemeraldine in its basic form has been found to be soluble in *N*-methylpyrrolidone (NMP)¹, in selected amines² and in sulfuric acid³. Processing from NMP solutions leads, however, to products which are non-conductive and require postdoping, for example through protonation with a sufficiently strong acid.

Very recently, it was discovered that protonation of polyaniline, if carried out with the use of an appropriate protonating agent, may induce solubility of the conducting form of polyaniline in common organic solvents such as toluene, chloroform, THF etc.⁴.

The concept behind this counterion-induced pro-

cessability requires some explanation. During the protonation of polyemeraldine base with an acid HA the counterion A⁻ is incorporated into the polymer matrix. If A⁻ contains a hydrophobic tail, as in the case of dodecyl benzene sulfonic acid (DBSA), it should facilitate the dissolution of the polymer in solvents commonly used in polymer solution processing. Indeed, several sulfonic acids were found to render polyaniline soluble in its doped (protonated) state⁴.

In principle, an increase in the number of appropriate functional groups of the counterion should lead to better processability of polyaniline. Among the obvious candidates as protonating agents, which would induce polyaniline solubility, are phosphoric acid diesters. Since phosphoric acid is a tribasic acid, its diesters should exhibit acidic properties while possessing two hydrophobic tails. Phosphoric acid esters are, in addition, known plasticizers for a variety of polymers⁵. Therefore, one is tempted to verify whether phosphoric acid diesters can act as protonating agents and simultaneously as plasticizers, thus enabling thermal processability of polyaniline in the same manner as for plasticized poly(vinyl chloride) (PVC).

In this paper we describe the protonation process of polyaniline with selected phosphoric acid diesters and discuss the properties of the obtained polymers including their processing properties.

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EXPERIMENTAL

Three esters were used: bis(2-ethylhexyl) hydrogen phosphate (DiOHP, diisooctyl hydrogen phosphate), bis(*n*-octyl) hydrogen phosphate (DnOHP) and bis(2-methylpropyl) hydrogen phosphate (DiBHP, diisobutyl hydrogen phosphate).

DiOHP was purchased from Aldrich (purity 97%) and used without further purification. DiBHP and DnOHP were prepared from POCl₃, the corresponding alcohols and water using a modification of the procedure described in ref. 6. Polyemeraldine base (PANI) was prepared by oxidative polymerization of aniline in the presence of HCl followed by deprotonation with 3 wt% aqueous solution of ammonia⁷. Protonations were performed by extended mixing of polyemeraldine base powder with neat diester. The diester/aniline mer ratios varied from 0.1 to 0.5.

I.r. spectra of protonated polyaniline were recorded on a Digilab FTIR spectrometer using KBr pellets. Differential scanning calorimetry (d.s.c.) studies were performed on a Mettler DSC 30 analyser. The samples of approximately 2 mg were sealed in air in an aluminium crucible. An empty aluminium crucible served as a reference. Thermogravimetric analysis measurements were carried out under a constant nitrogen flow using a Mettler TG 50 analyser. Mechanical tests were performed on an Instron 4501. Conductivities of the obtained films or pellets were measured using a conventional DC four-probe method with pressure contacts. Ohmic behaviour was tested in each case.

RESULTS AND DISCUSSION

Protonation studies

Polyaniline protonated with phosphoric acid diesters will be abbreviated here as PANI(DAHP)_y, where DAHP denotes the ester and *y* gives the fraction of the ester molecule per repeat polymer unit involving one ring and one nitrogen.

Neat DiOHP readily protonates solid polyemeraldine powder causing a drastic increase in its conductivity, which reaches 5 S cm⁻¹ (measured as pressed pellet) for

PANI(DiOHP)_{0.23}. For protonation levels above *y* = 0.25 abrupt plastification of the polymer occurs. The viscosity of the plasticized mixture decreases with the increase of *y*. It is not unexpected that DiOHP can act both as an excellent protonating agent and as a plasticizer. Phosphoric acid diesters show lower p*K*_a than the parent acid which is known to protonate PANI. On the other hand the alkyl tails in DiOHP have identical chemical structure to those of di(isooctyl) phthalate which is the most widely used plasticizer for PVC. The plastification at this low content of DiOHP is supposedly associated with branched substituents which increase the number of hydrophobic ends. DnOHP, which has linear substituents of the same stoichiometry as DiOHP, also plasticizes PANI but at *y* = 0.5; i.e., twice as much of the ester is required. Shorter chain diesters, such as for example DiBHP, plasticize PANI at even higher values of *y* (0.65).

Plasticized PANI(DiOHP)_y can be dissolved in several common solvents such as toluene, chloroform, THF etc. The soluble part of PANI(DiOHP)_y exhibits a green colour characteristic of the protonated state. In order to verify the stoichiometry of the dissolved phase, 500 mg of the plasticized PANI(DiOHP)_{0.3} was stirred in 3 ml of THF for 24 h. The soluble fraction was then separated by centrifugation and dried *in vacuo* at room temperature (RT). An identical experiment has been performed for PANI(DiBHP)_{0.3}. Elemental analysis of the soluble and insoluble parts was then performed. The results are summarized in Table 1. From these data it is evident that the soluble fractions are enriched in diesters as compared to the parent polymer. Consequently the non-dissolved parts contain less diester than the parent mixtures. This leads us to the conclusion that the percentage of the soluble fraction should increase with the increase of *y* in the parent film, which is also observed experimentally.

For the soluble fractions *y* ≥ 1, which means that more ester molecules are present in the system than there exist sites available for protonation (even considering both imine and amine sites of polyemeraldine) i.e. a fraction of DAHP must exist in the form of neutral free ester. The RT ³¹P spectrum of the soluble fraction of DiOHP-protonated PANI gives rise to a single line

Table 1 Elemental analysis of THF soluble and insoluble fractions of PANI(DiOHP)_{0.3} and PANI(DiBHP)_{0.3}

Elemental analysis of:		% Composition				
		C	H	N	P	O
PANI(DiOHP) _{0.3} soluble fraction	Calc. for PANI(DiOHP) _{1.0}	64.02	9.57	3.39	7.51	15.51
	Found	64.47	9.20	3.36	7.44	15.53
PANI(DiOHP) _{0.3} insoluble fraction	Calc. for PANI(DiOHP) _{0.22}	70.80	7.56	8.67	4.23	8.73
	Found	68.86	7.42	8.68	4.25	12.79
PANI(DiBHP) _{0.3} soluble fraction	Calc. for PANI(DiBHP) _{1.38}	53.64	8.07	3.68	11.24	23.22
	Found	53.06	7.71	3.49	10.70	25.04
PANI(DiBHP) _{0.3} insoluble fraction	Calc. for PANI(DiBHP) _{0.21}	68.47	6.32	10.40	4.83	9.98
	Found	66.69	6.18	9.77	4.56	12.80

with a chemical shift of 0.85 ppm, which is slightly lower than the observed chemical shift for free DiOHP (1.24 ppm). The change in chemical shift is consistent with protonation but it does not rule out the possibility of the coexistence of free ester and that bound via protonation. If the exchange of proton between free ester and its anion is sufficiently fast on the n.m.r. timescale one should observe only one n.m.r. line averaged for both coexisting species. Significant broadening of the n.m.r. line corroborates this hypothesis.

In Figure 1b the Fourier transform infra-red (FTi.r.) spectrum of the dissolved phase is presented. Its chain vibration modes are essentially the same as in the case of polyemeraldine protonated with HCl but additional bands characteristic of the ester functional groups are superimposed. In particular C–H stretching deformations characteristic of saturated aliphatic groups, P=O and P–O–R stretching vibrations are clearly visible (compare Figures 1a and 1b).

Thermal properties of plasticized PANI and its processability

D.s.c. curves of plasticized PANI(DiOHP)_y are very similar, independent of the value of y. They show one

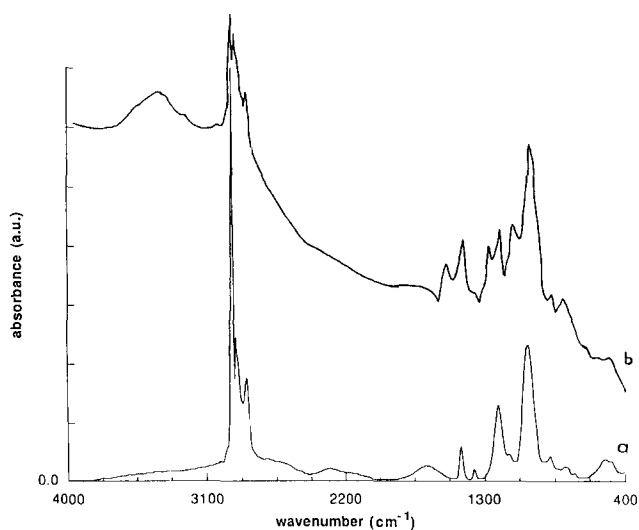


Figure 1 FTi.r. spectra of: (a) free DiOHP; (b) THF-soluble fraction of PANI(DiOHP)_{0.3}

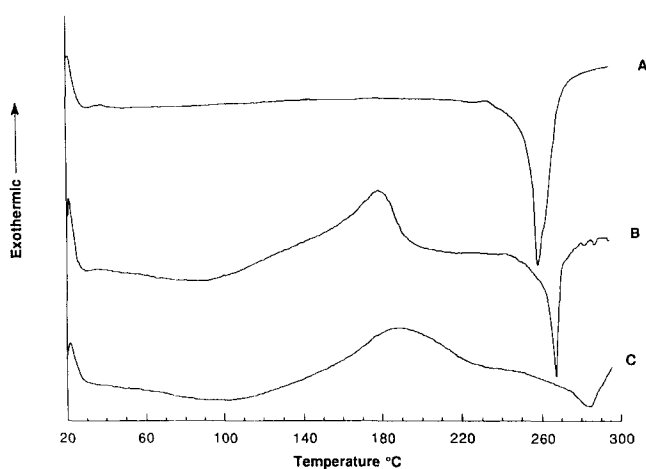


Figure 2 D.s.c. curves of PANI(DiOHP)_{0.4} at a heating rate of 10°C min⁻¹. Curve A: THF-soluble fraction; B, parent plasticized PANI(DiOHP)_{0.4}; C, THF-insoluble fraction

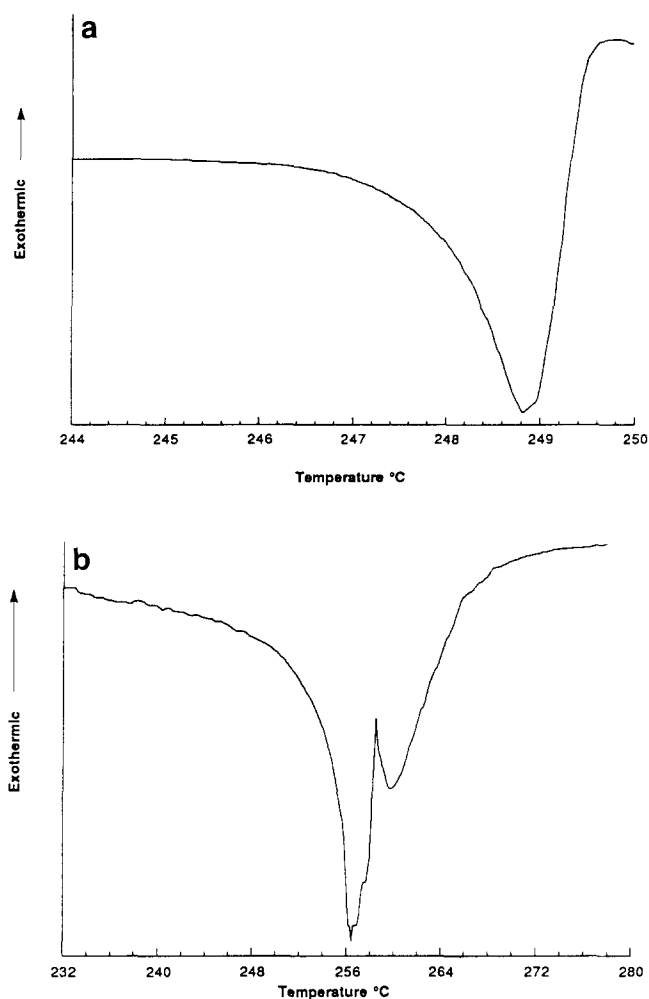


Figure 3 Endothermic decomposition peaks of (a) neat DiOHP; (b) THF-soluble fraction of PANI(DiOHP)_{0.4}

broad exothermic peak which starts at ~120–130°C and reaches a maximum around 180–190°C (Figure 2b). A sharp endothermic peak can be seen at 263°C. No mass loss is associated either with the exothermic or with the endothermic effects. It is interesting to compare the d.s.c. curves of THF-soluble fraction of PANI(DiOHP)_y and the insoluble fraction. To a first approximation, the d.s.c. curve of plasticized PANI(DiOHP)_y looks like a superposition of the d.s.c. traces of the soluble and the insoluble fractions (Figures 2a–c). The insoluble fraction shows a strong exothermic peak and a much weaker endothermic one whereas in the soluble fraction no heat effects can be observed up to 245°C, where the onset of a narrow endothermic peak can be observed. The endothermic peak is shown in detail in Figure 3b. In reality it consists of two partially overlapping peaks, the first at 257°C and the second at 262°C. The endothermic reaction is irreversible since in the second run no peaks are observed. Similarly, pure DiOHP does not show any heat effects up to 245°C, then it decomposes very abruptly at 249°C giving an extremely narrow endothermic peak (Figure 2a). Thus, the decomposition of the soluble fraction of PANI(DiOHP)_y is shifted by ~10°C with respect to pure DiOHP and occurs in two distinctly different steps. For parent PANI(DiOHP)_y and for its THF-insoluble fraction only one endothermic peak (coinciding with the higher temperature one for the soluble fraction) can be observed. It means that, in the

soluble fraction, the DiOHP is present in two different forms. This observation is consistent with the existence of two types of DiOHP in the soluble fraction of the polymer as postulated on the basis of analytical and n.m.r. data. Those ester molecules which do not participate in the protonation should be given off earlier since they are more loosely bound to the polymer matrix. It can be postulated that 'free' ester molecules solvate those which protonate PANI since phosphoric acid esters are known to form strong intramolecular hydrogen bonds⁸. Therefore the first endothermic peak would correspond to degradative desolvation. Ester molecules participating in the protonation would then be given off in the second step of degradation (second endothermic peak).

Plasticized PANI(DiOHP)_y is thermoprocessable and free-standing film can easily be formed by pressing at elevated temperatures. The preparation of films can be briefly outlined as follows: plasticized PANI(DiOHP)_y in the form of a disc of ~2 cm diameter and the thickness of a few millimetres was pressed between two aluminium sheets on a hot press at a given temperature. Both temperature and time of pressing were varied. The applied pressure in the majority of experiments was 100 MPa.

In Figure 4 the RT conductivities of the resulting films are plotted versus the temperature of pressing for samples with two different protonation levels, $y=0.23$ and $y=0.30$, the former corresponding to the onset of plastification and the latter to heavily plasticized material. The samples pressed below 140°C show conductivities exceeding 1 S cm⁻¹. For those pressed at lower temperatures, e.g. 100°C, conductivities up to 10 S cm⁻¹ can be obtained. It is interesting to note that a significant conductivity drop corresponds to the onset of the d.s.c. exothermic effect and is particularly significant for temperatures approaching the exothermic peak (compare Figures 2b and 4).

Some information concerning the nature of the degradation occurring in the vicinity of 160°C can be drawn from mechanical tests. The experiments can be briefly outlined as follows.

In all tests 100% s⁻¹ strain rate was applied. The stress-strain profiles depended mainly on the amount of the protonating-plasticizing agent (DiOHP). For low DiOHP contents ($y < 0.3$) the stress-strain profiles were

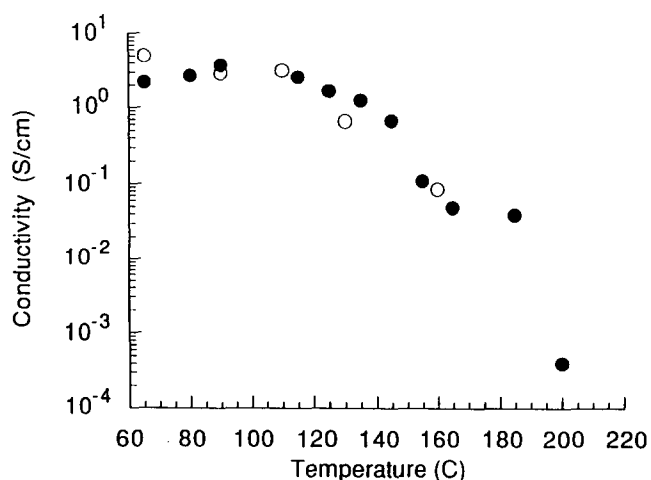


Figure 4 Conductivity versus pressing temperature for PANI(DiOHP)_y films obtained by hot pressing: (●) $y=0.23$; (○) $y=0.30$

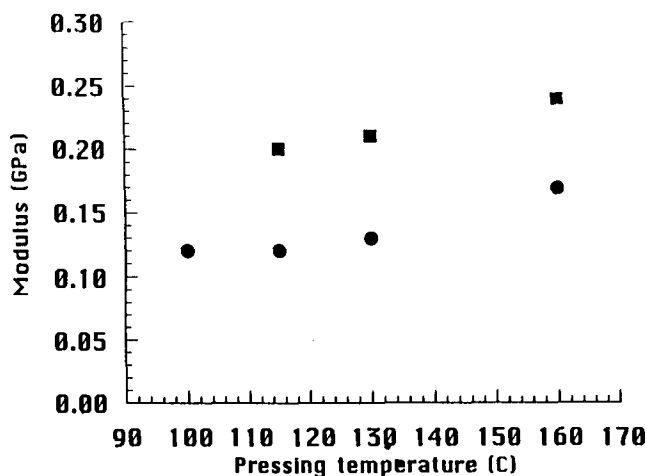


Figure 5 Modulus versus pressing temperature for PANI(DiOHP)_y films for a pressing time of 10 min. (●) $y=0.36$; (■) $y=0.33$

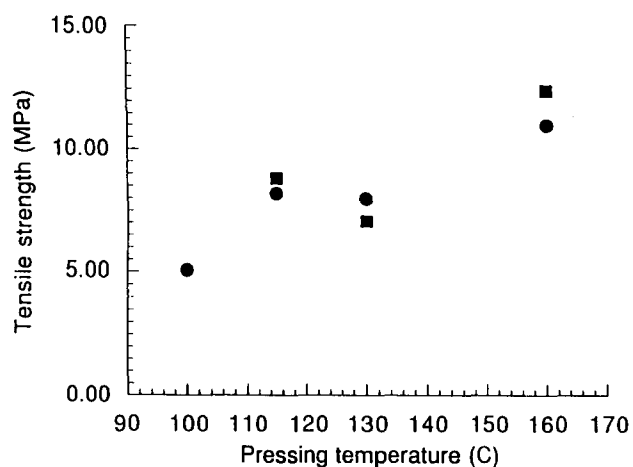


Figure 6 Tensile strength versus pressing temperature for PANI(DiOHP)_y films for a pressing time of 10 min. (●) $y=0.36$; (■) $y=0.33$

linear in the whole range. For more heavily plasticized samples the slope was initially linear and then $d\sigma/d\varepsilon$ began to decrease. However, no yielding was observed. The modulus values reported in this paper were derived from the initial linear part of the slope (initial modulus).

In Figure 5 the modulus versus temperature of pressing is plotted for two sets of PANI films with different DiOHP contents ($y=0.33$ and $y=0.36$). It is evident that the value of the modulus is determined by the plasticizing properties of the protonating agent and it strongly decreases even with a relatively small increase of the plasticizing agent content. For a given value of y the modulus is practically temperature independent up to 130°C. At the degradation temperature (160°C) the modulus and tensile strength increase (Figures 6 and 7), suggesting that the degradation process leads to the loss of the plasticizing properties of the ester. Furthermore, the degradation process might involve crosslinking rather than chain scission since in this last a decrease in the strength value should be expected.

Blends of plasticized PANI with plasticized PVC

DiOHP can act not only as a protonating agent and plasticizer for PANI but also plasticizes PVC as efficiently

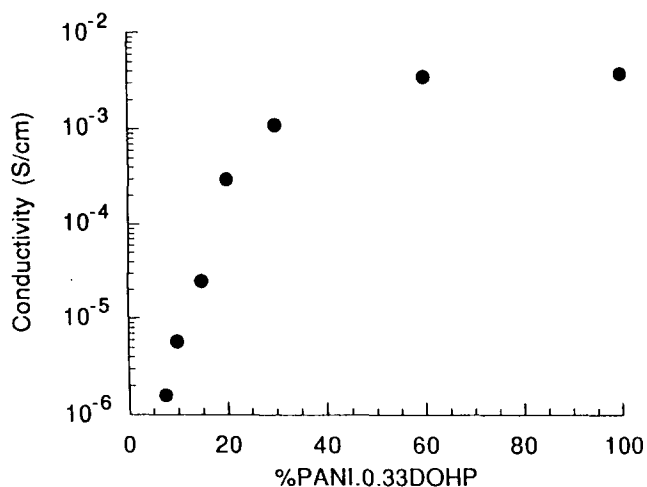


Figure 7 Conductivity versus PANI(DiOHP)_{0.33} content in plasticized PVC. Pressing temperature, 160°C; pressing time, 20 min

as di(isooctyl) phthalate. Therefore highly conducting composites of PANI and PVC can easily be obtained. For example, a plasticized mixture of composition 16.9 wt% PANI, 50.6 wt% PVC and 32.5 wt% DiOHP after hot pressing at 160°C shows conductivity as high as $1.1 \times 10^{-2} \text{ S cm}^{-1}$. However, DiOHP is acidic in nature and if it is not bound to polymer via protonation it may be corrosive. In the preparation of plasticized PANI-plasticized PVC blends it is therefore better to plasticize PANI with DiOHP and use a classical plasticizer for PVC, e.g. di(isooctyl) phthalate. In this case DiOHP will not be released from the polymer matrix because it quantitatively participates in the protonation of PANI.

Conducting blends of PANI with PVC were prepared as follows:

1. A plasticized mixture of PANI(DiOHP)_{0.33} was prepared by extended mechanical mixing of appropriate amounts of PANI and DiOHP at RT.
2. A plasticized PVC mixture was prepared separately by mixing 150 parts by wt of PVC, 50 parts by wt of di(isooctyl) phthalate and 60 parts by wt of CaCO₃.
3. Plasticized PANI and PVC mixtures were then mechanically mixed at RT for an extended period of time to achieve optimum homogeneity. Various plasticized PANI/plasticized PVC ratios were used.
4. The mixture containing PANI and PVC was then hot pressed at 160°C for 20 min.

The fabrication method described above results in very good mixing of plasticized PANI and PVC as demonstrated by microprobe studies and scanning microscopy.

In Figure 7 the RT conductivity is plotted versus the content of PANI(DiOHP)_{0.33} in plasticized PVC. The curve is rather typical of blends of conducting polymers with non-conducting matrices. A significant drop of the conductivity can be observed for PANI(DiOHP)_{0.33} contents lower than 20 wt%.

The effect of PANI(DiOHP)_{0.33} content in plasticized PVC matrix on the mechanical properties of the resulting polymer are shown in Figures 8 and 9. The tensile strength exhibits a clear minimum in the vicinity of 60 wt% PANI(DiOHP)_{0.33}, then its value slowly increases with decreasing content of the conducting phase. The

elongation at break is very low for high PANI(DiOHP)_{0.33} contents, whereafter it increases abruptly in the vicinity of the percolation threshold (Figure 10). These initial results show that reasonably conductive polyblends of good mechanical properties can be prepared from

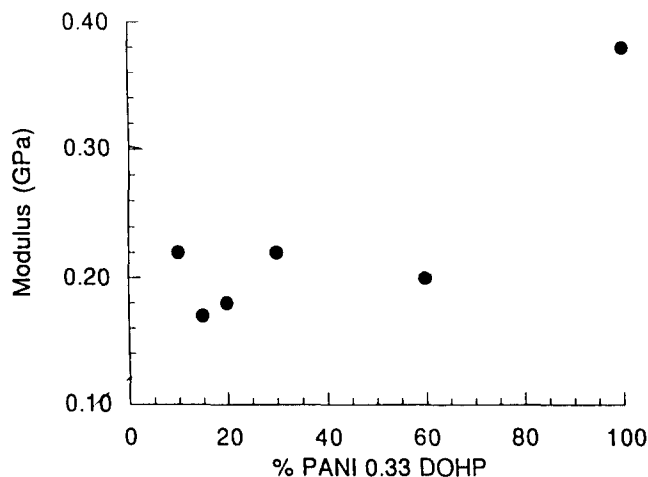


Figure 8 Modulus versus PANI(DiOHP)_{0.33} content in plasticized PVC. Pressing temperature, 160°C; pressing time, 20 min

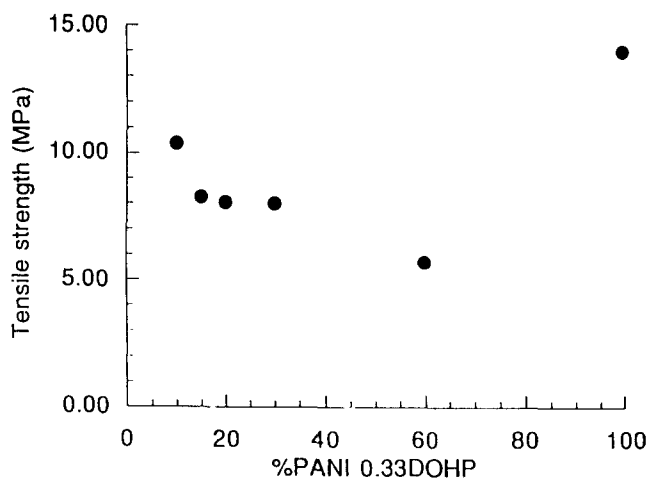


Figure 9 Tensile strength versus PANI(DiOHP)_{0.33} content in plasticized PVC. Pressing temperature, 160°C; pressing time, 20 min

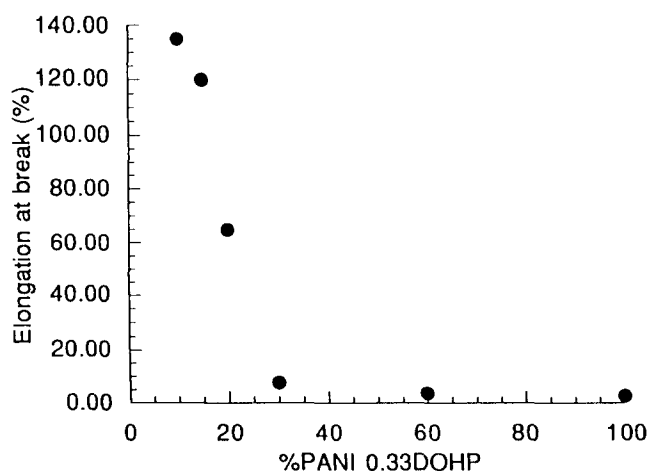


Figure 10 Elongation at break versus PANI(DiOHP)_{0.33} content in plasticized PVC. Pressing temperature, 160°C; pressing time, 20 min

plasticized PANI and plasticized PVC at 160°C, despite the fact that some degree of degradation of the blends is observed at this processing temperature.

CONCLUSIONS

To summarize, we have demonstrated that phosphoric acid diesters can act as excellent protonating agents for polyaniline. In particular, bis(2-ethylhexyl) hydrogen phosphate (or di(isooctyl) hydrogen phosphate DiOHP), in addition to protonation, effectively plasticizes conducting PANI at low ester contents – PANI(DiOHP)_y becomes plastic at $y > 0.25$. Plastification greatly facilitates processing of PANI. By hot pressing, free-standing conducting films of PANI(DiOHP)_y or its blends with PVC can easily be prepared.

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