

Miscibility of Conductive Blends of Poly(*o*-anisidine) with Poly(2-alkyl-2-oxazoline)s

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ABSTRACT: HCl-doped poly(*o*-anisidine) (PANIS-HCl) and undoped poly(*o*-anisidine) (PANIS-base) were blended with poly(2-methyl-2-oxazoline) (PMOx) or poly(2-ethyl-2-oxazoline) (PEOx) by solution casting from dimethyl sulfoxide. Blends containing 50 wt % or less of PANIS-HCl or PANIS-base were flexible and homogeneous. The glass transition temperature of the blend continuously shifted away from that of PMOx or PEOx with increasing PANIS-HCl or PANIS-base content, indicating miscibility. The shift in the T_g value was larger for the PMOx blend than for the corresponding PEOx blend, suggesting a stronger interpolymer interaction in the former blend. Fourier transform infrared spectroscopic studies indicated the presence of specific interactions in the blends as evidenced by the changes of C=O and NH bands. Blends containing 50 wt % of PANIS-HCl showed conductivity of about 10^{-4} S/cm. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 391–397, 1997

INTRODUCTION

Among the conducting polymers, polyaniline (PANI) is of particular interest due to its excellent air stability, low cost, and ease of polymerization, making it a potential candidate for many advanced technological applications.^{1,2} However, the commercial exploitation of these applications has been hampered by the poor processability of PANI. Thus, much effort has been directed toward the improvement of its processability.^{3–5}

The oxidation of *o*-anisidine (or *o*-methoxyaniline) in aqueous acid medium yields an electrically conductive polymer with interesting properties such as air stability and solubility in organic solvents.^{6,7} Unlike PANI, HCl-doped poly(*o*-anisidine) (PANIS) is soluble in some common organic solvents. The solubility of PANIS enables the preparation of conductive polymer blends by solution blending. MacInnes⁸ reported the preparation of blends of PANIS with some thermoplastics. A PANIS/polystyrene blend containing 5% of

PANIS was prepared by solution casting from *N,N*-dimethylformamide (DMF). The resulting film was strong but PANIS appeared not to be well dissolved as the film had a granular and particulate appearance. Binary blends of PANIS with poly(trimethyl hexamethylene terephthalate), nylon-66, or poly(butylene terephthalate) were also prepared by casting from trifluoroacetic acid or *N*-methylpyrrolidone. Blends containing more than 43% of PANIS were very brittle. Recently, Malmonge and Mattoso⁹ reported that flexible, free-standing, and stretchable films of PANIS/poly(vinylidene fluoride) can be prepared by solution blending. However, the miscibility of all these blend systems was not examined.

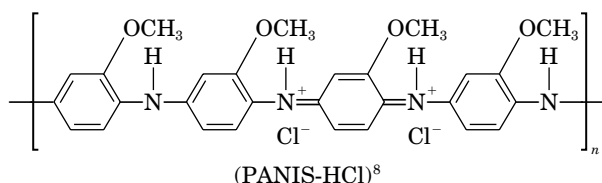
We recently reported that PANI doped with *p*-phenolsulfonic acid (PSA) is miscible with poly(vinyl acetate) (PVAc) and with poly(2-ethyl-2-oxazoline) (PEOx) up to 50 wt % of PANI-PSA through hydrogen-bonding interactions involving the carbonyl groups of the thermoplastic and the hydroxyl groups of PANI-PSA.^{10,11} In this communication, we report the miscibility of blends of PANIS with poly(2-methyl-2-oxazoline) (PMOx) and PEOx. Both the HCl-doped PANIS (PANIS-HCl) and the undoped PANIS base were used in

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this study. PMOx and PEOx were chosen as the blend components in view of the miscibility of PANI-PSA/PEOx blends. Both PMOx and PEOx have sufficiently low glass transition temperatures (T_g 's) such that they may serve as polymeric plasticizers to produce flexible and conductive polymer blends. We also reported that PMOx generally has a better ability to form miscible blends with other polymers than does PEOx.¹² It is of interest to study if the same trend is also observed in the present blend systems:



EXPERIMENTAL

Materials

o-Anisidine (from Merck) was double-distilled and stored under nitrogen in the dark prior to use. PANIS was prepared by oxidation polymerization. *o*-Anisidine (0.10 mol) was dissolved in 100 mL of a 1.0M HCl solution. A solution of K₂Cr₂O₇ (0.030 mol) dissolved in 200 mL of a 1.0M HCl solution was added dropwise to the monomer solution at 0–5°C. The mixture was continuously stirred for 20 h. Solid PANIS-HCl was filtered and washed with a 1.0M HCl solution followed by water to remove traces of the oxidant. The PANIS-HCl was then extracted with acetone to remove low molecular weight products. The PANIS-base was obtained by treatment of the extracted PANIS-HCl with 0.50M aqueous ammonia solution.

PMOx was prepared by ring-opening bulk polymerization as described previously.¹² PEOx was obtained from the Dow Chemical Co. The number- and weight-average molecular weights of PMOx and PEOx are 12,000 and 18,500, and 38,500 and 61,500 g/mol, respectively.

Binary blends of varying composition were prepared by solution casting from dimethyl sulfoxide (DMSO). DMSO solutions of PANIS-HCl (0.1% w/v), PANIS-base (0.1% w/v), PMOx (4% w/v), and PEOx (4% w/v) were separately prepared. Appropriate amounts of the solutions were then mixed. The well-mixed solution was transferred to an aluminum dish and allowed to dry *in vacuo*

at 50°C. The resulting film was further dried *in vacuo* at 90°C for 2 weeks.

Glass Transition Temperature Measurements

A TA instruments 2910 differential scanning calorimeter was used to determine the glass transition temperatures (T_g 's) of samples. Measurements were made using a heating rate of 20°C/min under a nitrogen purge of 60 mL/min. The initial inflection of the slope in the differential scanning calorimetry (DSC) curve was taken as T_g .

Fourier Transform Infrared (FTIR) Spectroscopic Measurements

FTIR measurements were made on a Perkin-Elmer 1600 FTIR spectrophotometer; 64 scans were signal-averaged at a resolution of 2 cm⁻¹. In view of the hygroscopic nature of PMOx and PEOx, spectra were acquired at 100°C using an SPCEAC high-temperature cell equipped with an automatic temperature controller.

Electrical Conductivity Measurements

Conductivity measurements were carried out on a four-point probe connected to a Keithley voltmeter constant-current source system. The conductivities were deduced based on at least 10 pairs of readings at different points on both sides of the samples.

RESULTS AND DISCUSSION

Thermal Characterization

DMSO is a suitable solvent for preparing PANIS blends. PANIS-HCl dissolves readily in DMSO to give an emerald green solution. On evaporating the solvent, brittle shiny film is obtained. Pellets made from the brittle film show conductivity similar to that of the untreated PANIS-HCl.

All the blends containing 5 wt % of PANIS-HCl or PANIS-base were green and transparent. Blends with higher PANIS content were dark in color but they appeared homogeneous. Blends containing 50 wt % or less of PANIS-HCl or PANIS-base were flexible. Blends containing 60 wt % or more of PANIS-HCl or PANIS-base were brittle and these blends were not further examined.

The T_g values of PMOx and PEOx as cast from DMSO are 65 and 55°C, respectively. The PMOx

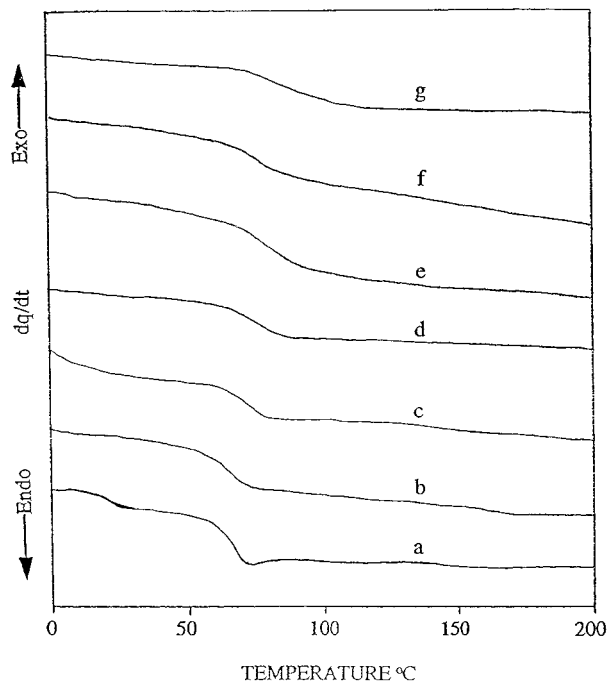


Figure 1 DSC curves of PANIS-HCl/PEOx blends: (a) 0; (b) 5; (c) 10; (d) 20; (e) 30; (f) 40; (g) 50 wt % of PANIS-HCl.

and PEOx samples for DSC measurements were dried under the same conditions as those of the blends. We were unable to detect with certainty the T_g s of PANIS-HCl and PANIS-base from their DSC curves. Pandey et al.¹³ reported a T_g value of 240°C for PANIS-base. However, their assignment of the glass transition appears doubtful as it is exothermic rather than endothermic and is complicated by the subsequent exothermic event. For PANI, Wei et al.¹⁴ reported that the T_g values measured by dynamic mechanical analysis were in the range of 140–220°C, depending on the residual solvent content in the cast film. It is reasonable to assume that the T_g values of PANIS-HCl and PANIS-base are also in this range. Thus, if PANIS-HCl and PANIS-base are miscible with PMOx or PEOx, the T_g value of the blend will shift away from that of PMOx or PEOx with increasing PANIS content.

Figures 1–4 show the DSC curves of the four blend systems. In all cases, the T_g value of the blend gradually shifts to a higher temperature with increasing PANIS content. A miscible blend is characterized by a single T_g with a value in between those of the two-component polymers. The gradual change in the T_g value and the homogeneous appearance of the blend are taken as an indication of miscibility. Tables I and II summarize the T_g results and the conductivities of vari-

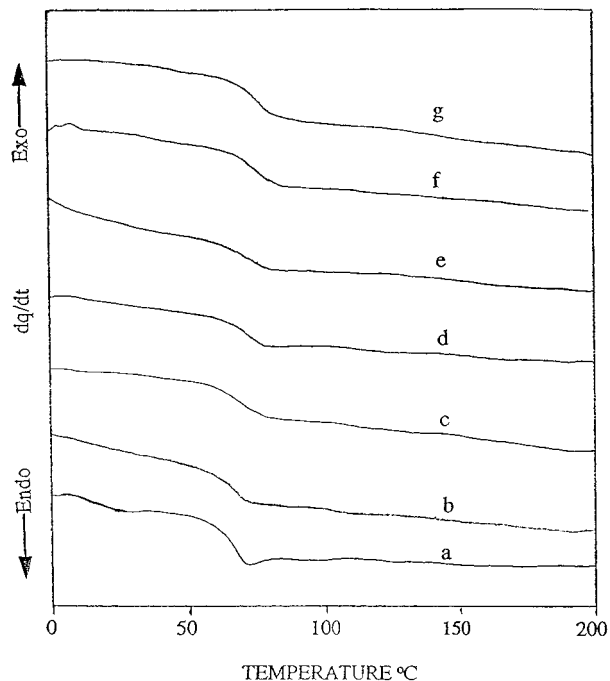


Figure 2 DSC curves of PANIS-base/PEOx blends: (a) 0; (b) 5; (c) 10; (d) 20; (e) 30; (f) 40; (g) 50 wt % of PANIS-base.

ous blends. The difference in the T_g values (ΔT_g) between the blend and PMOx or PEOx is also given. For most miscible polymer blends, the T_g -

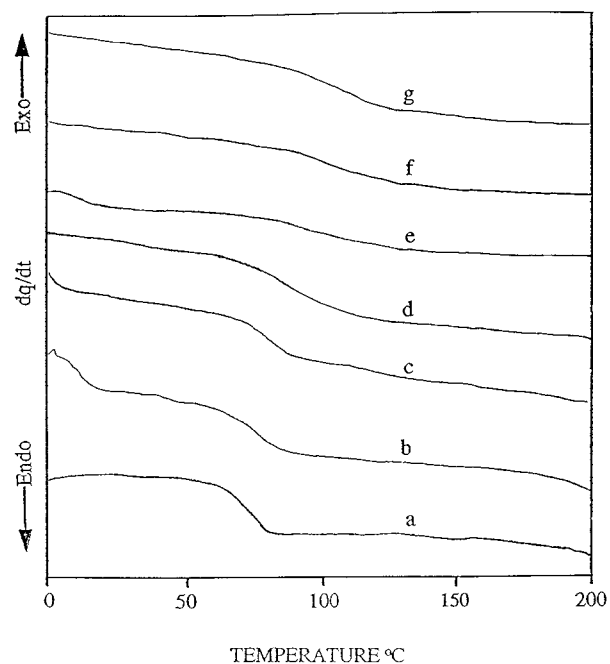


Figure 3 DSC curves of PANIS-HCl/PMOx blends: (a) 0; (b) 5; (c) 10; (d) 20; (e) 30; (f) 40; (g) 50 wt % of PANIS-HCl.

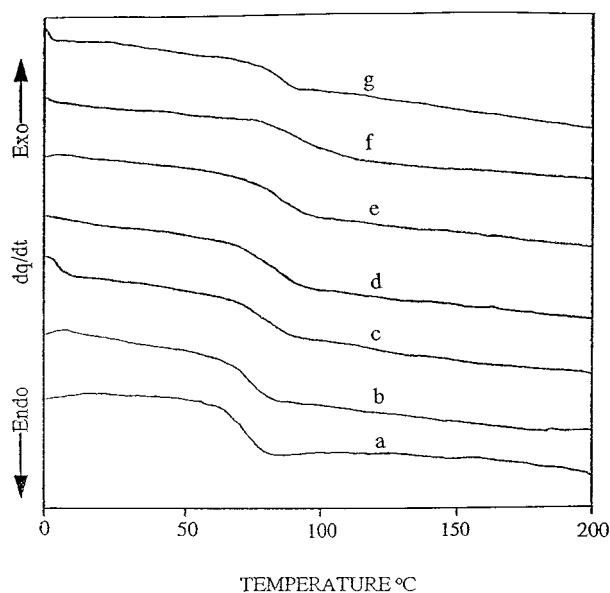


Figure 4 DSC curves of PANIS-base/PMOx blends: (a) 0; (b) 5; (c) 10; (d) 20; (e) 30; (f) 40; (g) 50 wt % of PANIS-base.

composition curves are concave. In other words, the T_g value of a blend is less than that calculated by the linear additivity rule. The concavity of the curve provides a qualitative measurement of interpolymer interaction in the blend. The more concave the curve, the less intense is the interaction.^{14–16} In cases where the two polymers are able to interact strongly through strong hydrogen bonding or ionic interaction, the T_g value of the resulting blend can then be larger than that predicted by the linear additivity rule.^{17,18} Although the T_g -composition curves of the present four systems are not constructed because the T_g values of PANIS-HCl and PANIS-base are not available, the ΔT_g values provide some clues on the concavity of the T_g -composition curves. The more concave the curve, the smaller is the ΔT_g value at a

given blend composition. The ΔT_g values of the PANIS-HCl/PEOx blends are of the same magnitude as those of PANIS/PEOx blends as reported previously.¹¹ It is interesting to note that the ΔT_g value is larger for the PANIS-HCl/PMOx blend than for the corresponding PANIS-HCl/PEOx blend. The results are then taken to indicate that PMOx interacts more strongly with PANIS-HCl than PEOx does and the indication is consistent with our earlier finding.¹²

It is also noted that the T_g shift of the PANIS-HCl blend is always larger than that of the corresponding PANIS-base blend. This can be an indication that PANIS-HCl shows better miscibility with poly(2-alkyl-2-oxazoline) than does PANIS-base. However, it is also possible that PANIS-HCl has a higher T_g value than that of PANIS-base, resulting from the presence of the chlorine counterions which stiffen the polymer chain.

FTIR Characterization

Miscibility of polymer blends generally arises from specific interactions between the component polymers. FTIR spectroscopy is commonly used to detect such interactions.^{19,20} Figure 5 shows the FTIR spectra in the carbonyl stretching region of various PANIS-HCl/PEOx blends. The carbonyl band of PEOx slightly broadens and gradually shifts toward lower frequency with increasing PANIS-HCl content in the blend. The frequency shift is about 5 cm^{-1} for a blend containing 30 wt % of PANIS-HCl. Similarly, for PANIS-base/PEOx blends, the carbonyl band of PEOx also shows a low-frequency shift upon blending with PANIS-base. The frequency shift is also about 5 cm^{-1} for a blend containing 30 wt % of PANIS-base.

Figure 6 shows the carbonyl bands of various PANIS-HCl/PMOx blends. The carbonyl band of

Table I Characteristics of PANIS-HCl/PMOx and PANIS-base/PMOx Blends

Composition (Wt % PANIS)	PANIS-HCl/PMOx			PANIS-base/PMOx	
	T_g (°C)	ΔT_g (°C)	Conductivity (S cm^{-1})	T_g (°C)	ΔT_g (°C)
5	67	2	1.5×10^{-6}	67	2
10	72	7	5.3×10^{-6}	71	6
20	77	12	6.5×10^{-6}	74	9
30	81	16	9.6×10^{-6}	77	12
40	84	19	2.2×10^{-5}	79	14
50	86	21	8.6×10^{-5}	81	16

Table II Characteristics of PANIS-HCl/PEO_x and PANIS-base/PEO_x Blends

Composition (Wt % PANIS)	PANIS-HCl/PEO _x			PANIS-base/PEO _x	
	T_g (°C)	ΔT_g (°C)	Conductivity (S cm ⁻¹)	T_g (°C)	ΔT_g (°C)
5	58	3	1.6×10^{-6}	57	2
10	61	6	4.7×10^{-6}	59	4
20	62	7	6.2×10^{-6}	61	6
30	63	8	8.9×10^{-6}	62	7
40	64	9	3.1×10^{-5}	63	8
50	66	11	7.2×10^{-5}	63	8

PMO_x slightly broadens and shifts toward lower frequency with increasing PANIS-HCl content. For a blend containing 30 wt % of PANIS-HCl, the frequency shift is about 7 cm⁻¹, which is slightly larger than that observed for the corresponding PANIS-HCl/PEO_x. This can be taken as an indication of a stronger interaction between PMO_x and PANIS-HCl than that between PEO_x and PANIS-HCl. Similar band broadening and a frequency shift of the carbonyl band in PANIS-base/PMO_x blends are also observed, but the spectra are not shown here.

In contrast to the subtle changes of the carbonyl band, the NH band of PANIS shows significant changes upon blending with PMO_x or PEO_x.

Figure 7 shows the FTIR spectra in the NH stretching region of various PANIS-HCl/PEO_x blends. For PANIS-HCl (curve a), the band at 3378 cm⁻¹ is attributed to the free NH groups. The band at 3331 cm⁻¹ is attributed to weakly self-associated NH groups. The band at 3250 cm⁻¹ represents a distribution of stronger hydrogen bonds possibly formed between the —NH— and —N= groups as suggested by Furukawa et al.²¹ for PANI. Upon blending with PEO_x, the intensity of the bands at 3378 and 3331 cm⁻¹ decreases while that of the hydrogen-bonded band at 3250 cm⁻¹ increases. The results show that more NH groups have participated in intermolecular interactions upon the addition of PEO_x. Moreover, the

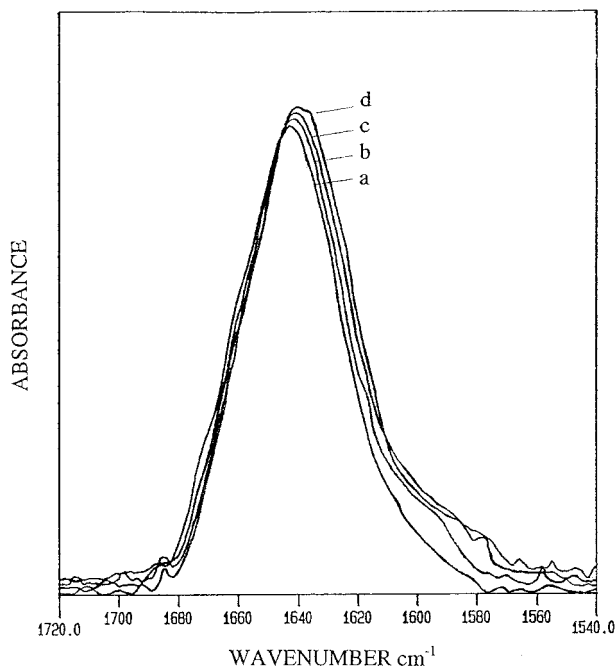


Figure 5 FTIR spectra in the carbonyl region of PANIS-HCl/PEO_x blends: (a) 0; (b) 10; (c) 20; (d) 30 wt % of PANIS-HCl.

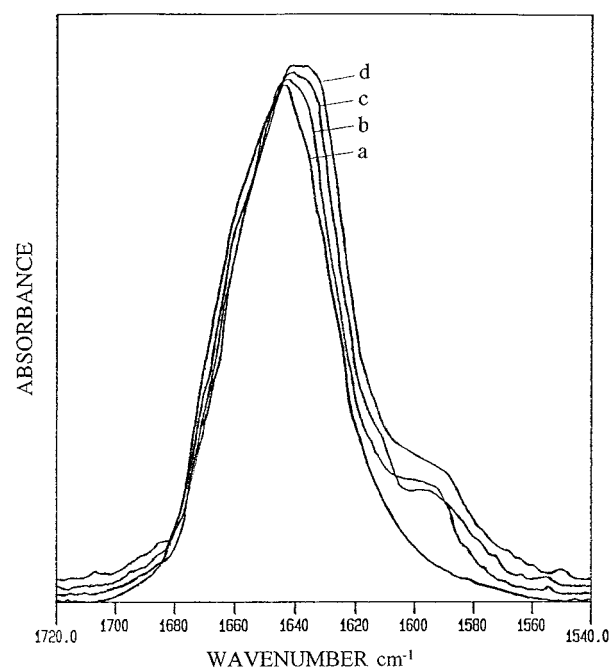


Figure 6 FTIR spectra in the carbonyl region of PANIS-HCl/PMO_x blends: (a) 0; (b) 10; (c) 20; (d) 30 wt % of PANIS-HCl.

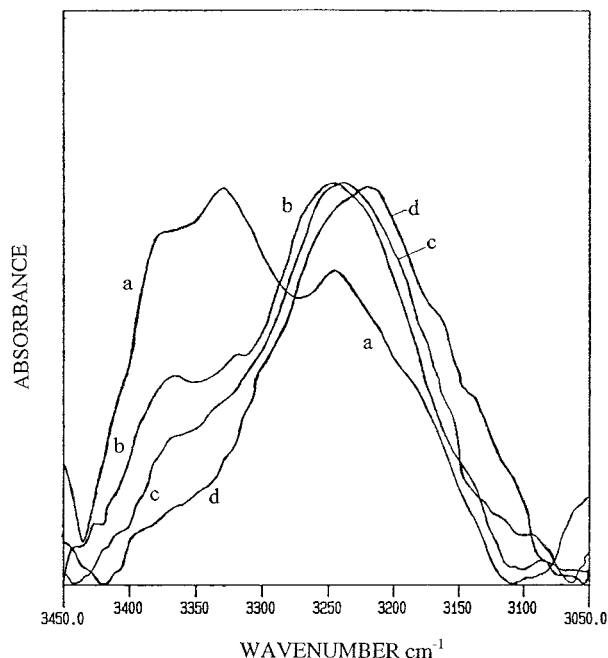


Figure 7 FTIR spectra in the NH stretching region of PANIS-HCl/PEOx blends: (a) 100; (b) 40; (c) 30; (d) 20 wt % of PANIS-HCl.

center of the hydrogen-bonded NH band gradually shifts to lower frequency with increasing PEOx content. For a blend containing 20 wt % of PANIS-HCl, the center is located at 3221 cm^{-1} , representing a frequency shift of 29 cm^{-1} .

Figure 8 shows the FTIR spectra in the NH stretching region of various PANIS-HCl/PMOx blends. Similar to the PEOx system, the addition of PMOx also leads to a reduction in the intensity of the bands at 3378 and 3331 cm^{-1} and an increase in the hydrogen-bonded NH band. The frequency shift of the hydrogen-bonded band is larger than that of the corresponding PEOx blend. For example, a blend containing 20 wt % of PANIS-HCl shows a frequency shift of 45 cm^{-1} from 3250 to 3205 cm^{-1} . The frequency shift of the corresponding PEOx blend is 29 cm^{-1} , as mentioned earlier. The larger frequency shift of the PMOx blends once again shows that PMOx interacts more intensely with PANIS-HCl than does PEOx.

The NH bands of PANIS-base in both PANIS-base/PEOx and PANIS-base/PMOx blend systems also show similar changes but the frequency shift of the hydrogen-bonded NH band is slightly smaller than that of the corresponding PANIS-HCl blend. For instance, a shift of 40 cm^{-1} from 3250 to 3210 cm^{-1} is observed for a PANIS-base/PMOx blend containing 20 wt % of PANIS-base.

Thus, PANIS-HCl interacts more intensely with poly(2-alkyl-2-oxazoline) than does PANIS-base. Such a stronger interaction is also responsible for the larger T_g shifts of the PANIS-HCl blends as mentioned earlier.

Conductivity Measurements

The conductivities of various blends are shown in Tables I and II. The PANIS-HCl/PMOx blend and the PANIS-HCl/PEOx blend of the same composition show similar conductivity. However, the conductivity of PANIS-HCl/PEOx blend is lower than that of the previously reported PANI-PSA/PEOx blend.¹¹ For example, a PANIS-HCl/PEOx blend containing 50 wt % of PANIS-HCl shows a conductivity of $7.2 \times 10^{-5}\text{ S/cm}$ while the corresponding PANI-PSA/PEOx blend shows a conductivity of $1.7 \times 10^{-3}\text{ S/cm}$. The lower conductivity of the PANIS-HCl blends is due to the low intrinsic conductivity of PANIS-HCl which has a conductivity of $1.1 \times 10^{-3}\text{ S/cm}$. The ring conjugation in PANIS may be decreased due to the steric interference between the ortho-substituent and the neighboring hydrogen.

CONCLUSIONS

Flexible and miscible blends of PANIS with PMOx or PEOx up to 50 wt % of PANIS can be obtained

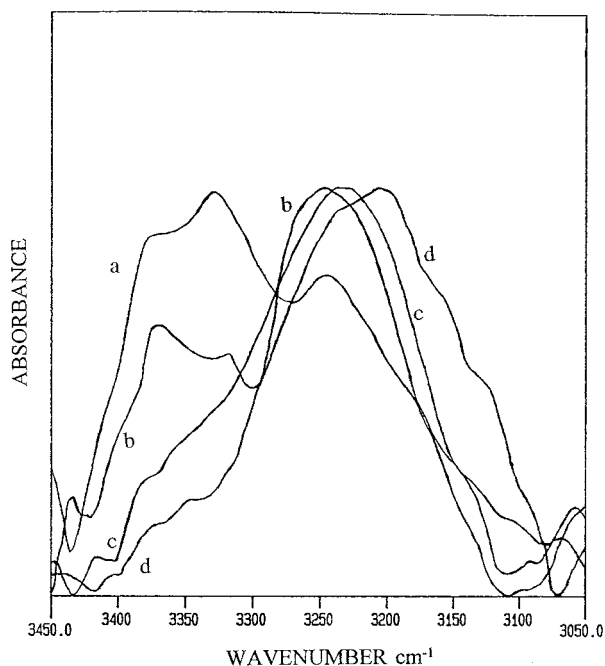


Figure 8 FTIR spectra in the NH stretching region of PANIS-HCl/PMOx blends: (a) 100; (b) 40; (c) 30; (d) 20 wt % of PANIS-HCl.

by solution casting from DMSO. FTIR studies show the existence of interactions between PANIS and poly(2-alkyl-2-oxazoline). DSC and FTIR measurements indicate that PMOx interacts more intensely with PANIS than does PEOx.

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