

polymer papers

Liquid-crystalline solutions of electrically conducting polyaniline

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Polyaniline (PANI), fully protonated with camphor sulfonic acid (CSA), was found to form liquid-crystalline solutions in *m*-cresol. The existence of this interesting state of matter was inferred from observations of opalescence, depolarization of plane-polarized light and the existence of a critical concentration for the onset of the formation of the liquid-crystalline phase. This critical concentration was found, in accord with existing theory, to decrease monotonically as the viscosity or molecular weight of the polyaniline increased. By shearing the liquid-crystalline solutions onto glass substrates and subsequent precipitation in acetone, oriented polyaniline films were obtained. The existence of a liquid-crystalline phase implies a rather rigid conformation of the fully protonated polyaniline in solution. Importantly, the emeraldine base form of PANI remained isotropic in solutions in *m*-cresol up to very high concentrations. Thus it is suggested that protonation induces a chain stiffening and extension of the polyaniline macromolecules (relative to the insulating emeraldine base) resulting from a combination of electronic delocalization and counter-ion 'crowding'.

(Keywords: polyaniline; liquid-crystalline solutions; electrically conducting polymers)

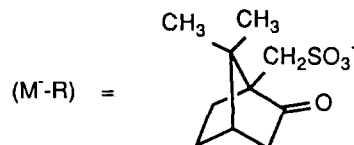
INTRODUCTION

Although polyaniline (PANI) has been investigated since the beginning of this century¹ it is only recently that this polymer has attracted interest as a conducting material². Its wide range of desirable electrical, electrochemical and optical properties, coupled with excellent environmental stability, make PANI potentially attractive for use as an electronic material in a variety of applications.

In the past, PANI has been categorized as an intractable polymer. Recently, however, several methods has been reported to dissolve and process PANI in, for example, *N*-methylpyrrolidinone (NMP)³, pyrrolidine or tripropylamine⁴ or in concentrated sulfuric acid and other strong acids^{5,6}. More recently we reported⁷ that high molecular weight polyaniline can be doped to the conducting form and, simultaneously, dissolved in common non-polar or weakly polar organic solvents, which further enhances its processibility.

In the latter case, dissolution and processing of polyaniline in its conducting form in common organic solvents is made possible by doping with functionalized protonic acids. These functionalized protonic acids are generically denoted $H^+(M^-R)$, where the counter-ion species (M^-R) contains a functional group R that is chosen to be compatible with non-polar or moderately polar organic liquids. An important example^{7,8} is

camphor sulfonic acid (CSA), where



After doping and complexing with CSA, the resulting conducting PANI complex can be processed from solution in a wide variety of solvents; and cast into free-standing films, or spun into fibres, with room-temperature electrical conductivities^{7,8} in the remarkably high range of 200–400 S cm⁻¹.

In our earlier studies⁷ PANI doped with functionalized protonic acids and their blends with common bulk polymers were processed from relatively dilute solutions (2–8% w/w of PANI salt). An important aspect of the counter-ion-induced solubility of polyaniline is that, with selected protonic acids, conducting PANI can be dissolved to very high concentrations (as high as 40% w/w, depending on the molecular weight) in specific organic solvents. One might expect that the fully protonated, conducting PANI macromolecule would have a relatively rigid character in solution due to the π -electron delocalization along the polymer chain. This feature fulfils one important requirement for the formation of liquid-crystalline solutions, as is observed, for example, for aramides⁹. Obviously, the occurrence of liquid crystallinity in polyaniline systems would be of

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interest from both a scientific and an industrial point of view.

In this paper we report the observation of the formation of liquid-crystalline solutions of conducting polyaniline and summarize the results obtained for the optical anisotropy and the critical concentration for the onset of lyotropic behaviour of polyanilines of different polymer molecular weights, doped with CSA, in solutions in *m*-cresol. Some initial results on the formation of oriented films derived from liquid-crystalline PANI solutions are also presented.

EXPERIMENTAL

Samples of PANI of different molecular weights were prepared by standard polymerization in aq. HCl solution, initiated by ammonium persulfate¹⁰, and by emulsion polymerization of aniline in xylene¹¹. The resulting polyaniline salts were compensated with 3% aq. ammonium hydroxide for 2 h and subsequently washed with water, methanol and acetone and then dried at 50°C for 24 h. The inherent viscosities of emeraldine base samples were determined at 25°C in 0.1% w/w solutions in concentrated sulfuric acid (97%), using an Ubbelohde viscosimeter.

The different emeraldine base samples were mixed at room temperature with (\pm)-10-camphor sulfonic acid (Aldrich) in a molar ratio of 0.5:1 (CSA to phenyl-N (PhN) repeat unit of PANI), using an agate mortar and pestle in an inert atmosphere to yield the fully protonated emeraldine salt form. An appropriate quantity of the resulting complex was mixed with *m*-cresol to prepare solutions of different concentrations. The mixtures of PANI-CSA and *m*-cresol were placed into a double-helix mixing apparatus and mixed at room temperature for 24 h, during which time the complex dissolved to yield viscous, dark-green solutions.

The critical concentration for the onset of liquid crystallinity was determined by preparing a series of PANI-CSA/*m*-cresol solutions of concentrations at 5% v/v intervals (or at 2.5% intervals in the vicinity of the critical concentration region) using PANI emeraldine base samples from each batch of different inherent viscosity. The critical concentration was taken to be the lowest PANI-CSA concentration above which a fluid, birefringent phase appeared. All observations were made using a Nikon Microphoto-XFA polarizing optical microscope.

Transmission electron microscopy was carried out with a JEOL 100 CX instrument operated at 80 kV.

RESULTS AND DISCUSSION

As reported previously^{7,8}, the PANI-CSA complex can be dissolved in *m*-cresol over a very wide concentration range to form homogeneous, deep-green solutions. In these *m*-cresol solutions, polyaniline is in the protonated, conducting form, as was inferred from the absorption spectrum of the PANI-CSA complex¹² and from the Pauli temperature-independent magnetic susceptibility¹³.

We observed that highly concentrated solutions of PANI-CSA in *m*-cresol were optically anisotropic; i.e. they depolarized plane-polarized light. *Figure 1a* shows a micrograph of a thin layer of 21% v/v PANI-CSA solution in *m*-cresol, taken between crossed polarizers of an optical microscope (CSA/PhN = 0.5; inherent viscosity

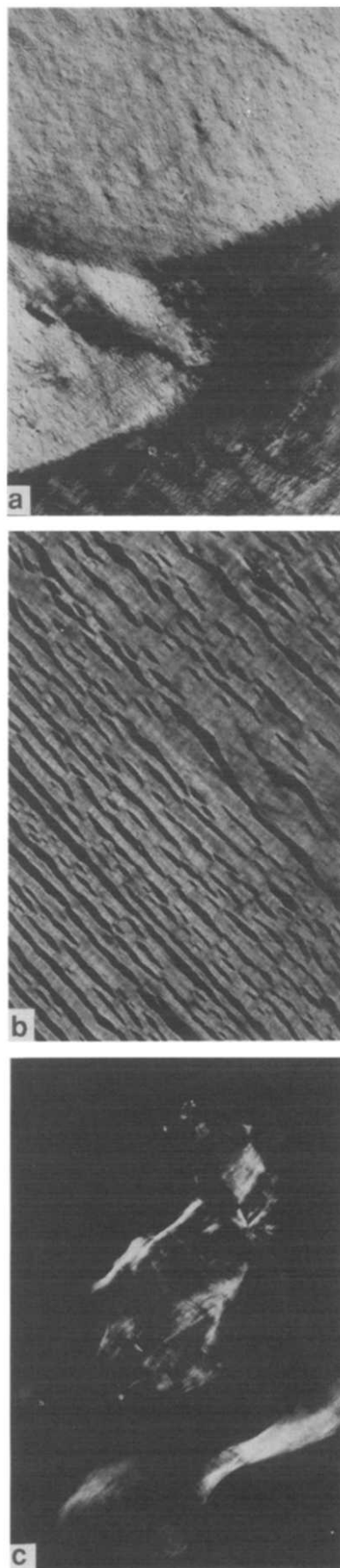


Figure 1 (a) Thin layer of liquid-crystalline solution of 21% v/v PANI-CSA ($\eta_{inh} = 1.2 \text{ dl g}^{-1}$) in *m*-cresol. (b) Same solution sheared by sliding the cover slip in the direction perpendicular to the visible (dark) striations. (c) Thin layer of 17.5% v/v solution of PANI-CSA ($\eta_{inh} = 1.2 \text{ dl g}^{-1}$) in *m*-cresol displaying an anisotropic phase surrounded by isotropic (dark) region; crossed polarizers

of emeraldine base $\eta_{\text{inh}} = 1.2 \text{ dl g}^{-1}$). The photomicrograph in this figure reveals that the solution exhibited anisotropic domains, which were found to have mobile boundaries, and some threadlike features. These anisotropic solutions retained directional character from weak shear; i.e. after smearing a solution onto a substrate (cf. *Figure 1b*). With decreasing concentration of PANI-CSA in *m*-cresol, a two-phase system became apparent (*Figure 1c*). This figure illustrates the appearance of small anisotropic domains against the dark background of the isotropic phase in a 14.5% v/v solution of PANI-CSA ($\eta_{\text{inh}} = 1.2 \text{ dl g}^{-1}$) in *m*-cresol. Any further decrease of the concentration of PANI-CSA in *m*-cresol at room temperature leads to a complete disappearance of the anisotropic phase. In the case of emeraldine base of $\eta_{\text{inh}} = 1.2 \text{ dl g}^{-1}$ it was found that a 13.5% v/v solution was completely isotropic. When this solution was gently stirred, however, opalescence was observed.

The critical concentration for the onset of stable anisotropy in lyotropic solutions is expected to vary with molecular weight¹⁴. *Figure 2* shows the measured critical concentration of PANI-CSA in *m*-cresol as a function of the inherent viscosity of the emeraldine base samples used. This graph clearly illustrates that when PANI of lower η_{inh} , i.e. of lower molecular weight, was used, a higher concentration of PANI-CSA was required to cause the formation of an anisotropic solution. We note that an emeraldine base of the same inherent viscosity but prepared by different polymerization procedures (chemical polymerization in aqueous solution¹⁰ or emulsion polymerization in non-polar organic solvents¹¹) yielded identical critical concentrations.

The observed increase of the critical concentration with decreasing molecular weight is in accord with classical theory^{15,16}. According to the lattice theory of Flory¹⁶, the threshold volume fraction V^* for the appearance of a stable anisotropic phase in a solution of rods of axial ratio x can be expressed as

$$V^* \approx (8/x)[1 - (2/x)] \quad (1)$$

At high values of x this expression further reduces to:

$$V^* \approx 8/x \quad (2)$$

In order to compare the present experimental results with the above relations the value of x needs to be

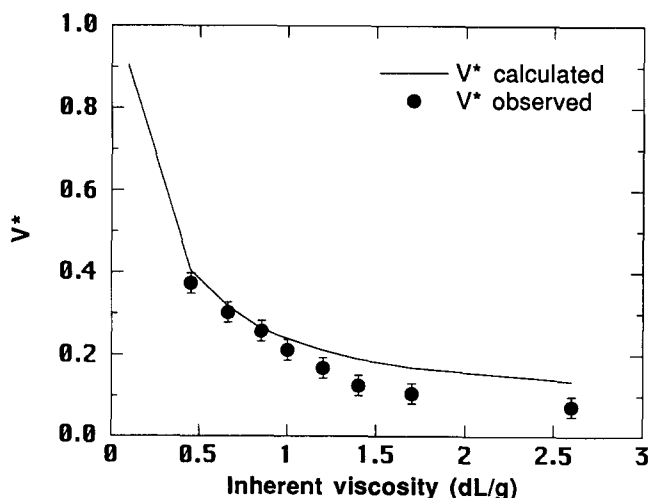


Figure 2 Critical volume fraction, V^* , for formation of anisotropic phase versus inherent viscosity η_{inh} of emeraldine base. Solid line is calculated according Flory's expression (equation (1), see text)

Table 1 Molecular weights of emeraldine base samples calculated according to equations (3) and (4) and estimated from size-exclusion chromatography data

η_{inh} (dl g^{-1})	M_w (kg kmol^{-1})		S.e.c. ^a
	Calculated		
	Flexible chain (equation (3))	Rigid chain (equation (4))	
0.18	4400	4500	
0.45	15 000	8800	
0.66	25 000	11 640	5700
0.85	35 000	14 000	9000
1.00	43 500	15 800	
1.20	55 400	18 000	11 200
1.40	68 100	20 200	13 300
1.66	85 500	23 000	14 300
2.62	296 200	28 700	

^a At 25°C in concentrated H_2SO_4

estimated from the polyaniline chain length and its effective diameter. Due to a lack of knowledge of the chain conformation of PANI in solution, the molecular weight cannot be directly derived from viscosity data. In an earlier paper⁶ we estimated the upper and lower limits of the molecular weights of PANI from viscosity measurements by comparing the data with viscosities obtained under identical conditions for nylon 6 (as the coiled chain conformation limit) and for poly(*para*-phenylene terephthalamide) (PPTA) (as the rigid chain limit). The Mark-Houwink relations for these polymers in sulfuric acid solutions at 25°C are reported to be^{17,18}

$$[\eta] = 3.32 \times 10^{-4} M_w^{0.75} \quad \text{for nylon 6} \quad (3)$$

$$[\eta] = 1.95 \times 10^{-6} M_w^{1.36} \quad \text{for PPTA} \quad (4)$$

where the unit of the intrinsic viscosity $[\eta]$ is dl g^{-1} . The accordingly estimated upper and lower limits of the molecular weights of the polyaniline used in this work are listed in *Table 1*. For comparison, we also show in this table the molecular weights of some of the polyaniline samples as derived from size-exclusion chromatography (s.e.c.) analysis in solution in sulfuric acid and calibrated against PPTA.

Earlier e.s.r. experiments on solutions of polyaniline salt in organic solvents¹³ suggested that the macromolecular conformation of polyaniline salt in solution is relatively rigid. This is, of course, consistent with the present observation of liquid-crystalline behaviour in concentrated solutions. Thus, using the molecular weights deduced according to equation (4) for chains with a PPTA-like conformation, we estimated the axial ratio x of the different polyaniline samples assuming that the repeat length of two aniline units is 7.15 Å and that the effective diameter of PANI-CSA is 20 Å. The latter value was derived from X-ray diffraction data of oriented thin films of PANI-CSA¹⁹. From the values of x , and the densities of the various components (1.034 and 1.28 g cm^{-3} for *m*-cresol, and the PANI complex, respectively), the critical concentration V^* was calculated with relation (1) for polyaniline salt in solution in *m*-cresol. The predicted critical concentrations for the onset of a stable liquid crystalline phase of polyanilines of different inherent viscosities (solid line) are shown in *Figure 2*. As can be seen in this graph, the theoretically predicted critical concentrations are in accord with the measured values.

This agreement confirms the rod-like conformation of the protonated polyaniline macromolecules in solution.

It is worth pointing out that the emeraldine base form of PANI could be dissolved without difficulty in *m*-cresol to yield first a homogeneous *blue* solution which later became *greenish* after prolonged storage; or more quickly upon mild heating. The colour change was obviously due to protonation of PANI by *m*-cresol which acted as a weak protonic acid. However, no transition to the anisotropic phase was observed in these solutions even at concentrations of emeraldine base ($\eta_{inh} = 1.2 \text{ dl g}^{-1}$) in *m*-cresol as high as 20% v/v. This observation suggests that the emeraldine base had a more flexible chain conformation in solution in *m*-cresol. Apparently, complete protonation by strong acids was essential for transforming the polyaniline chains from flexible coils to

more rigid entities and, consequently, for the formation of liquid-crystalline solutions of polyaniline.

We suggest that the chain stiffening and extension of the conducting emeraldine salt form of polyaniline, relative to the insulating emeraldine base or not fully protonated salt, resulted from a combination of electronic delocalization and counter-ion 'crowding'. Since the protonated form of PANI has a half-filled electronic band it has the electronic structure of a metal. Coiling of the chain would cause considerable disorder along the chains and thereby localize the electronic wave functions; thus, electronic delocalization naturally favours a more rigid chain conformation^{20,21}. Molecular models of the PANI-CSA complex suggest that additional stiffening resulted from crowding of the CSA counter-ions bound to the PANI chains. The importance of the latter (crowding) contribution to the chain stiffness was also derived from the observation that PANI protonated with, and dissolved in, concentrated sulfuric acid (which is of significantly smaller size) was not found to display lyotropic behaviour in the concentration range studied.

We additionally investigated the effect of excess CSA (i.e. CSA/PhN molar ratios > 0.5) on the critical concentration for the formation of liquid-crystalline solutions of PANI in *m*-cresol. It was found that at an increasing molar ratio of CSA to polyaniline repeat unit the critical concentration of total salt in *m*-cresol systematically increased. However, the emeraldine base content in those anisotropic solutions was essentially identical. This suggests that additional CSA did not further change the conformation of CSA-doped polyaniline in solution in *m*-cresol, and that complete protonation (CSA/PhN = 0.5) was sufficient to change the conformation of the polyaniline chains from flexible coils to more rigid chains.

When a small quantity of anisotropic PANI-CSA solution was sheared between two glass slides and then quickly dipped into acetone highly anisotropic, green PANI-CSA textures were obtained (Figure 3a). A fibrillar structure was formed in which the polyaniline macromolecules were aligned with the fibril axis along the direction of shear (cf. the electron diffraction pattern of Figure 3b). The properties of such oriented systems derived from lyotropic solutions of PANI will be presented elsewhere.

CONCLUSION

Concentrated solutions of conducting PANI, doped with camphor sulfonic acid, in *m*-cresol, display liquid crystalline behaviour above a critical concentration. The existence of a liquid-crystalline phase was inferred from opalescence and depolarization of plane-polarized light. The dependence of the critical concentration for the onset of the formation of this phase on the molecular weight of the PANI was in excellent agreement with that expected for rigid macromolecules. Shearing of liquid-crystalline solutions onto a substrate and subsequent precipitation of PANI-CSA yielded oriented, conducting polyaniline films.

The existence of the liquid-crystalline PANI phase is indicative of a rod-like chain conformation of fully-protonated polyaniline in solution, as inferred earlier from e.s.r. measurements. The discovery of liquid-crystalline behaviour of polyaniline solutions provides a deeper understanding of polyaniline as a soluble conducting polymer. Moreover, such liquid-crystalline

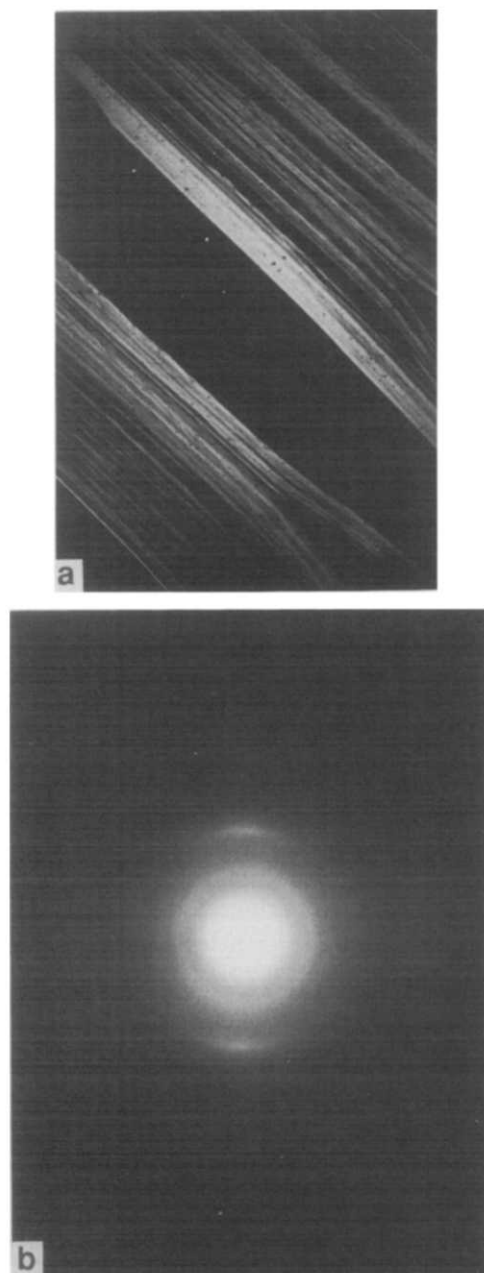


Figure 3 (a) Optical micrograph of thin PANI-CSA film derived from an anisotropic 21% v/v PANI-CSA solution ($\eta_{inh} = 1.2 \text{ dl g}^{-1}$) in *m*-cresol, by sliding the cover slide and subsequent precipitation in acetone; crossed polarizers. (b) Electron diffraction pattern of precipitated film; direction of shear was horizontal

solutions are potentially useful for the preparation of highly oriented fibres and films with enhanced electrical and mechanical properties.

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REFERENCES

- 1 Green, A. G. and Woodhead, A. E. *J. Chem. Soc.* 1910, 2388
- 2 MacDiarmid, A. G., Chiang, J.-C., Halpern, M., Mu, W.-L., Somasiri, N. L. D., Wu, W. and Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* 1985, **121**, 173
- 3 Angelopoulos, M., Asturias, G. E., Ermer, S. P., Ray, A., Scherr, E. M. and MacDiarmid, A. G. *Mol. Cryst. Liq. Cryst.* 1988, **160**, 151
- 4 Han, C. C., Shacklette, L. W. and Elsenbaumer, R. L. Symposium on 'Electric, Optical and Magnetic Properties of Organic Solid State Materials', 1991 Fall Meeting of The Materials Research Society, Boston, MA, 2-6 December 1991, p. 105
- 5 Andreatta, A., Cao, Y., Chiang, J.-C., Smith, P. and Heeger, A. J. *Synth. Met.* 1988, **26**, 383
- 6 Cao, Y., Smith, P. and Heeger, A. J. *Synth. Met.* 1989, **32**, 263
- 7 Cao, Y., Smith, P. and Heeger, A. J. *Synth. Met.* 1992, **48**, 91
- 8 Cao, Y., Treacy, G. M., Smith, P. and Heeger, A. J. *Appl. Phys. Lett.* 1992, **60**, 2711
- 9 Morgan, P. W. *Macromolecules* 1977, **10**, 1381
- 10 Cao, Y., Andreatta, A., Heeger, A. J. and Smith, P. *Polymer* 1989, **30**, 2305
- 11 Österholm, J.-E., Cao, Y., Klavetter, F. and Smith, P. Abstract of ICSM '92, to be published in *Synth. Met.*
- 12 Cao, Y., Smith, P. and Heeger, A. J. Abstract of ICSM '92, to be published in *Synth. Met.*
- 13 Cao, Y. and Heeger, A. J. *Synth. Met.* 1992, **52**, 193
- 14 Kwolek, S. L., Morgan, P. W., Schaeffgen, J. R. and Gulrich, L. W. *Macromolecules* 1977, **10**, 1390
- 15 Onsager, L. *Ann. N. Y. Acad. Sci.* 1949, **51**, 627
- 16 Flory, P. J. *Proc. R. Soc., London Ser A* 1956, **234**, 60
- 17 Baird, D. G. and Smith, J. K. *J. Polym. Sci., Polym. Chem. Edn* 1978, **16**, 61
- 18 Kamade, K. and Yukio, M. *Kobunshi Ronbunshu* 1978, **35**, 467
- 19 Yang, C. Y., Smith, P. and Heeger, A. J. Unpublished data
- 20 Pincus, P. A., Rossi, G. and Cates, M. E. *Eur. Phys. Lett.* 1987, **4**, 41
- 21 Spiegel, D., Pincus, P. and Heeger, A. J. *Polym. Commun.* 1988, **29**, 264