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Electrical conductivity enhancement of predoped polyaniline by stretch orientation

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A method for the reproducible production of isotropic free standing camphorsulfonic acid doped polyaniline with a conductivity of (300 ± 30) S cm^{-1} is described. The paper then goes on to describe a method of stretch orienting such films to enhance the conductivity parallel to the draw direction to (890 ± 30) S cm^{-1}. This improvement is attributed to orientation of both the crystal and amorphous phases. The samples produced by this method are the first stress oriented predoped polyaniline specimens reported in the literature. Copyright © 1996 Elsevier Science Ltd.

(Keywords: deformation of camphorsulfonic acid doped polyaniline; orientation; conductivity enhancement)

Introduction

At the moment there is a great deal of commercial interest in being able to replace metallic E-M shields with a cheap, easily processable alternative; however, a conductivity of about 1000 S cm^{-1} is required to meet the most stringent shielding standards. Investigation of a number of polymers has shown that doped polyaniline (PANi) is the most promising material to fulfil this application[1], being air stable, cheap to produce on an industrial scale, and most importantly processable[2].

The first breakthrough in the development of PANi came when Angelopoulos *et al.*[3] found that good freestanding films of the insulating emeraldine base form of polyaniline could be produced using *N*-methyl-2-pyrrolidone (NMP) as a solvent.

These films were stretch oriented[4] and then doped using post process acidification to render the polymer films conductive[5]. It is difficult, however, to achieve homogeneous doping in a dense film. This procedure gave isotropic films with a conductivity of 75 S cm^{-1} and drawn samples with conductivities up to 350 S cm^{-1}, which is well below the useful value.

The problem of efficient post process doping has been circumvented by the discovery of acid solution processing routes to produce free standing, processable, highly conductive films ('predoping', the second breakthrough). These were first described by Cao *et al.*[6] using two specific functional acids, (±)-10-camphorsulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA) in various organic solvents. One particular system, PANi:CSA in *meta*-cresol (*m*-cresol), produces isotropic free standing films with conductivities of 100–300 S cm^{-1} which exhibit metallic-like transport properties[7]; in fact this system can be classified as a disordered metal near the metal–insulator boundary and so has become the focus of a great deal of research with the objective of understanding the physics of a conductive polymer.

Ward and co-workers[8] have shown over the last two decades that the physical and mechanical properties of classical, processable polymers, such as polyethylene can be enhanced by deforming the polymer. The improvement observed has been attributed to orientation of the polymer chains within both the crystalline and amorphous phases. Using a similar argument, Fischer *et al.*[9] showed that the increase in conductivity in stretch oriented NMP cast polyaniline (post process doped) was due to the nucleation of a small amount of new crystalline material rather than growth and/or orientation of any pre-existing crystallites, and orientation of the amorphous phase. It is the aim of this communication to show that deformation of predoped polyaniline is also possible and that it allows the conductivity of PANi:CSA to be enhanced to nearly an industrially usable level by orientation of both the crystalline and amorphous phases.

Experimental

Stress orientation of PANi:CSA is not a trivial task; to stand any chance of success, good quality isotropic feed stock with a thickness variation of less than 5% is imperative. The production of this material will now be discussed.

High molecular weight PANi base was prepared at −25°C using the synthesis route described by Adams *et al.*[10]. Avylanov *et al.* [11] have suggested that films with the highest conductivities can be obtained by protonating all the imine sites with CSA (50% of the nitrogen sites), thus free standing 50% doped PANi:CSA films were prepared in the following manner. The emeraldine base was mixed with CSA in a molar ratio of (1 : 0.5) in a mortar and pestle to obtain the 'fully' protonated conducting emeraldine salt form. This was then dissolved in an appropriate amount of a dry 1 : 1 mixture of *m*-cresol and chlorobenzene (an antigelation agent) to obtain a 1.6% polymer solution. The mixture was then dispersed using an Ultra-Turrax T25 homogeniser for approximately 15 min at 20 000 rpm before being poured onto a polished

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silicon wafer and then dried at 60°C under a dynamic vacuum for 20 h.

Even after this drying period, it is believed that about 15% of the weight of samples cast using only CSA and *m*-cresol (i.e. no chlorobenzene) is due to retention of the solvent; just like NMP is retained in NMP cast films[12] (incomplete drying), and it is thought that this acts as a plasticiser 'softening' the samples. The chlorobenzene was initially added to the solution to prevent gelation during mixing; however, it was also found to produce samples which were more ductile than samples manufactured using just *m*-cresol. Thus some of the chlorobenzene is also retained and provides further plasticization.

Removal of as much water and other impurities from the reagents as possible was found to improve isotropic film quality and conductivity more than longer, slow mixing. The use of this processing route increased the conductivity of the isotropic feed stock from (100 ± 60) to $(300 \pm 30)\,\mathrm{S\,cm^{-1}}$, and gave isotropic films with a thickness of $(80 \pm 4)\,\mu$m.

Dumbbell shaped specimens with a gauge aspect ratio of 6 were then guillotined from the feed stock to provide high quality edges. This prevents failure due to tearing from defects on the edges of the specimens. Some initial differential scanning calorimetry studies have shown that the glass transition temperature of PANi:CSA is approximately 145°C, thus the deformation temperature was chosen to be 150°C so that the samples would be ductile due to the increased free volume. Attempts to draw samples at lower temperatures have all failed at low strains (< 25% extension).

The specimens were deformed using an Instron 4505 tensile testing machine which had been preheated to 150°C for 1 h and then checked with a Comark digital thermometer to ensure that there was no temperature deviation > 0.5°C anywhere in the oven as hot or cold spots could lead to sample failure. Fiducial markers were drawn onto the surface of the sample at 3 mm intervals using a marking jig and a fine, soft, fibre tip pen so the amount of deformation parallel to the draw direction could be determined by taking the ratio of line displacement after and before sample deformation. The specimens were then placed, in turn, into the oven where they were left until the oven reached thermal equilibrium. Thermogravimetric analysis of a typical sample shows that (5 ± 2)% of the sample's weight was lost during this period due to loss of *m*-cresol and chlorobenzene. As 15–20% of the as cast sample's weight is due to retention of *m*-cresol and chlorobenzene, sample 'hardening' due to removal of the plasticizers during the thermal emersion before stretching should not be a significant problem.

The specimens were then deformed uniaxially at a rate of $5\,\mathrm{mm\,min^{-1}}$, a strain rate of $0.2\,\mathrm{min^{-1}}$. Once the deformation of each specimen was complete, the oven door was opened, and the sample was allowed to cool to room temperature under load so that any orientation was frozen into the sample.

The conductivity parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the draw direction, in the plane of the film, were then found using a four-in-line probe[13]. The samples were then left to age for 2 months at room temperature before the conductivities were remeasured. The values obtained at the different ages were found to agree within experimental error. The measured conductivity values, and the anisotropies calculated from these are plotted against extension in *Figures 1* and *2*. The 2θ diffraction pattern of a single specimen of the isotropic sample was collected using a Philips diffractometer and CuK_{α} radiation in reflection.

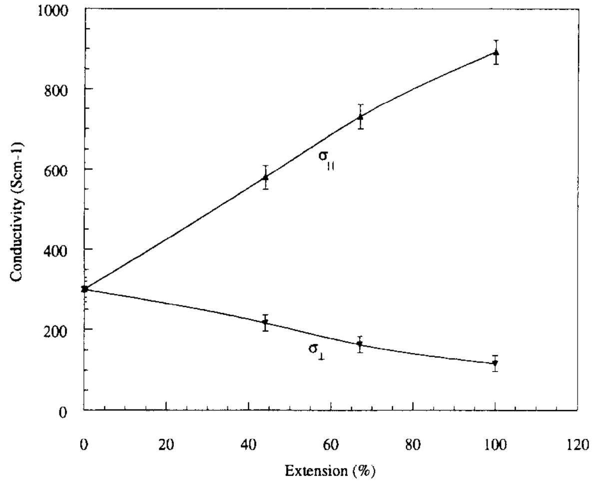

Figure 1 Effect of deformation on the conductivity of predoped polyaniline: ▲, conductivity parallel to the draw direction; ▼, conductivity perpendicular to the draw direction

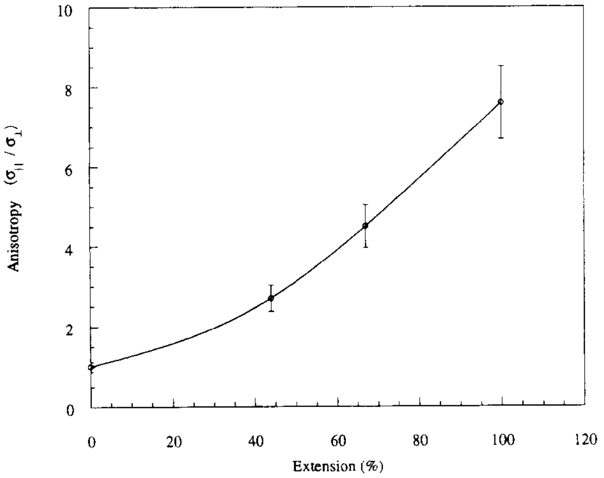

Figure 2 Deformation induced anisotropy of predoped polyaniline

Texture induced in a drawn sample can be studied using 4 circle X-ray diffraction techniques; in this work a single specimen of the 67% stretched sample was studied using a Huber goniometer with CuK_{α} radiation. This technique relies on the fact that the measured intensity after corrections is proportional to the number of crystallographic plane normals (axes) or 'poles' which are parallel to the scattering direction, a reference direction which bisects the angle between the source and detector and lies in the plane formed by the source, detector and sample. Thus the orientation distribution of a chosen set of (*hkl*) crystallographic planes can be measured by fixing the detector at the appropriate 2θ angle so that it receives radiation scattered from these planes and then rotating the sample, the scan is parameterized by defining two spherical angles. The angle between the scattering direction and the sample plane normal is defined as α, and the angle between the projection of the scattering direction onto the sample and the symmetry axis of the sample perpendicular to the

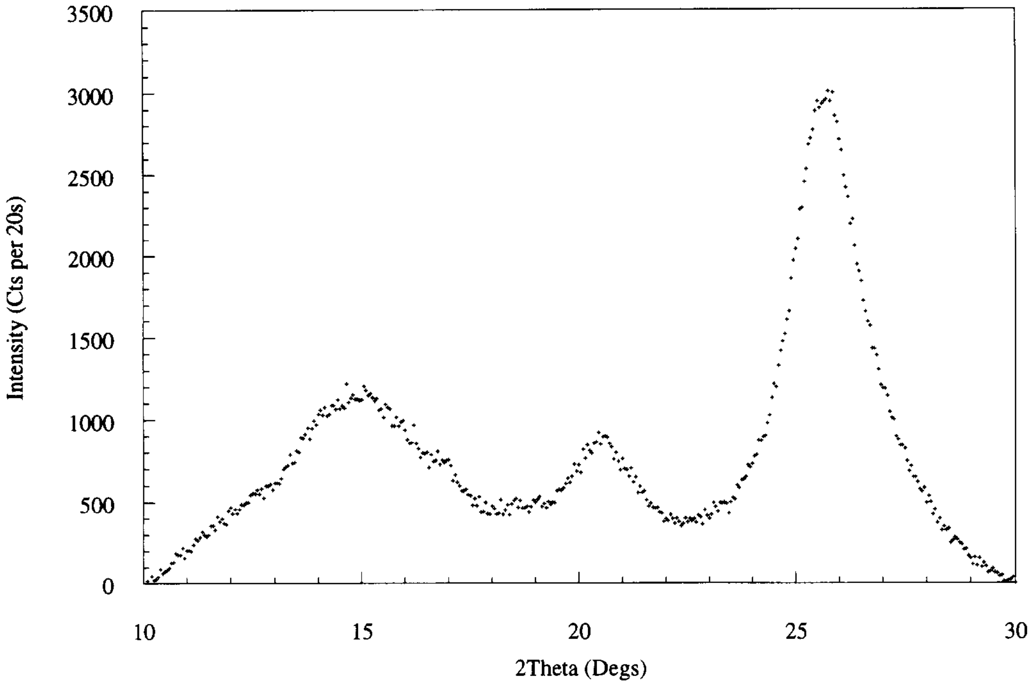

Figure 3 Plot of a 2θ diffractometer scan of an isotropic polyaniline sample

draw direction and in the plane of the film (the transverse direction) is defined as β.

Brief summary of results

The plot of conductivity against extension shown in *Figure 1* indicates that it is possible to enhance the electrical conductivity parallel to the draw direction of the aligned films by uniaxially deforming CSA doped polyaniline. The highest conductivity so far obtained is $890\,\mathrm{S\,cm^{-1}}$, which is very close to the desired useful conductivity. The 2θ diffractometer scan of the isotropic film (see *Figure 3*) shows that films made via the CSA:*m*-cresol route have a higher crystallinity than films produced via the NMP route[9]. Thus the big difference in conductivities (and temperature dependent transport properties[14]) of isotropic doped films made by the two methods could be explained if the crystalline phase had a different transport mechanism and hence a much higher conductivity than the amorphous phase.

A comparison of the 2θ diffractometer scans of the isotropic and drawn samples (as shown in *Figures 3* and *6*), which have been corrected for thickness and any geometrical effects, at $\alpha = 0°$ shows that there is a decrease in scattering from *both* the amorphous phase and the equatorial crystalline reflection at $2\theta = 25.5°$ (the poles of which lie in the *a–b* plane of the unit cell) of the drawn sample. Little change is observed in the crystalline peak at $2\theta = 20.75°$, and no new diffraction peaks are observed due to the production of a new crystal structure within the range $2\theta = 2–100°$. This behaviour of the crystallites is unexpected if uniaxial orientation is occurring, with the chain axis orienting towards the draw direction. In this case one would expect orientation of the *a–b* crystallographic axes (which are themselves randomly oriented about the *c* crystallographic axis) into the plane formed by the transverse direction and normal to the plane of the film (normal–transverse plane). Some orientation and crystallization of the amorphous regions may also be expected. Thus for uniaxial orientation an increase in scattering from the crystalline reflections accompanied by a decrease in scattering from the amorphous phase is expected. Alternatively any decrease in crystallinity should be accompanied by an increase in scattering from the amorphous phase due to destruction of crystalline order during processing. A decrease in scattering from *both* phases suggests the development of preferred orientation away from $\alpha = 0°$ and crystallization/orientation of the amorphous phase. To check this, an α scan with the scattering direction in the normal–transverse plane ($\beta = 0°$), and a β scan with the scattering direction in the plane of the film ($\alpha = 90°$) of the $2\theta = 25.54°$ peak, the equatorial reflection showing the biggest effect, were performed. The results are presented in *Figures 4* and *5*, respectively. *Figure 5* shows that the poles of this reflection are orienting into the normal–transverse plane which is consistent with the crystallographic *c* (or chain) axes orienting towards the draw direction, as expected. *Figure 4*, however, shows that there is a preferred direction at $\alpha = 10°$. To check this further additional 2θ scans were taken at $\alpha = 10°$

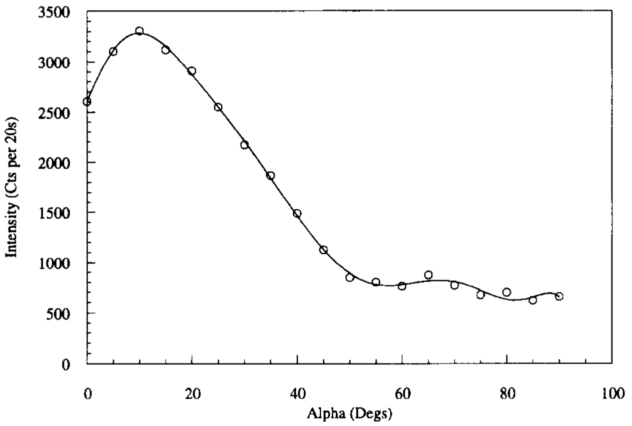

Figure 4 Alpha scan of drawn predoped polyaniline

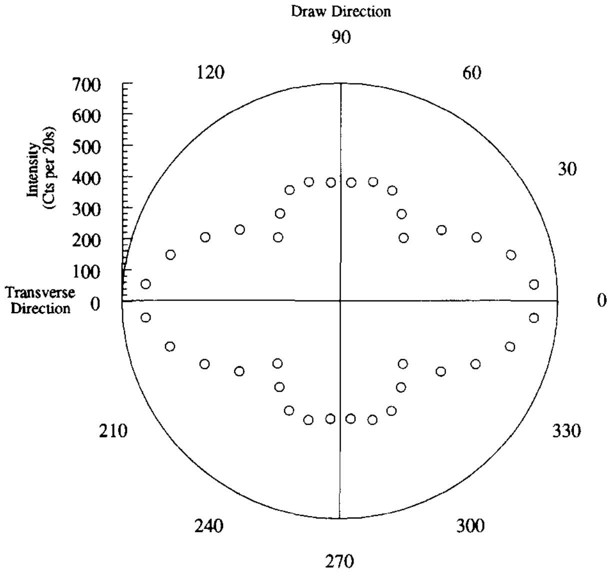

Figure 5 Beta scan of drawn predoped polyaniline

and 90°, these are shown in *Figure 6*. It can be seen from this that the intensity of scattering from the crystal phase increases and then decreases which supports the idea of non-uniaxial orientation of the crystallites developing. The peak in *Figure 4* corresponds to scattering from crystal planes which are oriented at 10° to the plane of the film.

Some initial work on indexing the X-ray diffraction peaks of PANi:CSA indicates the presence of a very nearly cubic lattice[15], thus the increase in conductivity could be due to the development of oriented lamellar, with the chain axes parallel to the draw direction and a plane which lies at 10° to the plane of the film. This we feel may represent a plane formed by the phenylene rings along the polymer backbone as a 10° tilt angle for this 'phenylene ring' plane is consistent with the calculated tilt angle in the salt form calculated by Baughman *et al.*[16] after being flattened by the presence of bulky CSA groups[17].

A number of interesting observations can also be made from *Figures 3* and *6*. The broad peak due to scattering off the amorphous phase occurs approximately 5° lower in these CSA:*m*-cresol samples than Fischer *et al.*[9] found in their NMP cast samples and changes in intensity in the drawn samples in the same way, but not in proportion to, the crystalline phase; this could be attributed to the induction of some orientation and short range order in the amorphous phase, which could also improve the conductivity of the amorphous phase. Examination of *Figure 3* indicates that each peak is actually a combination of two or more peaks due to scattering from more than one crystal phase. This supports the idea suggested by Cao *et al.*[18] that more than one crystal structure is possible in this material. *Figures 3* and *6* also indicate that these orient at the same rate and the unit cell dimensions and crystallite sizes remain fixed during deformation as the peak positions and half widths of the crystalline reflections do not change in these scans. A parallel study[19] indicates that the amount of doping affects the amount of each phase present, and actually seems to give the highest conductivity at 60% doping which can be attributed to the best compromise between doping of the nitrogen sites and development of a particular 'highly conducting' crystal structure. A more detailed study of the structure and orientation development of the crystalline and amorphous phases is currently underway[15], thus refinement of the doping level and drawing conditions will hopefully allow higher conductivity values to be obtained in the near future.

Conclusions

This paper demonstrates that a relatively small amount of deformation of predoped PANi:CSA leads to a three-fold increase in the electrical conductivity parallel to the draw direction to 890 S cm^{-1}. Some initial

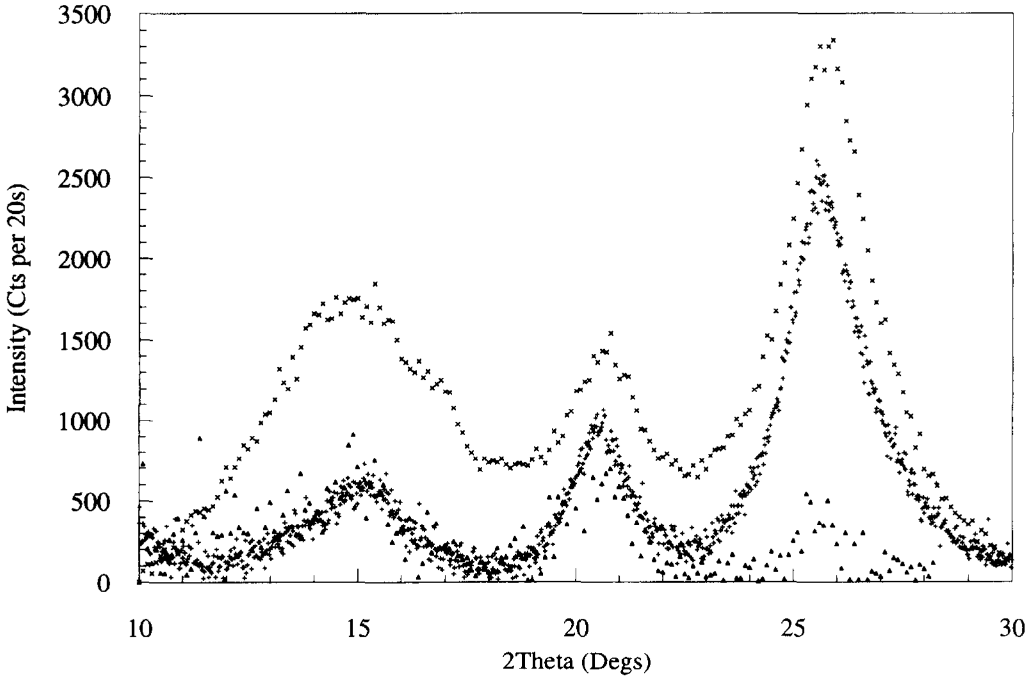

Figure 6 Plot of 2θ diffactometer scans of drawn predoped polyaniline samples at $\alpha = 0°$ (+), 10° (×), 90° (▲) with $\beta = 0°$

X-ray work indicates that this can tentatively be attributed to orientation of both the crystalline and amorphous phases.

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