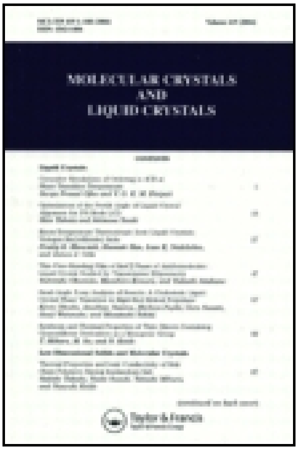

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High Performance Fibers of Conducting Polymers

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High Performance Fibers of Conducting Polymers

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We present a summary of our recent results on the electrical and mechanical properties of fibers made from poly(2,5-dimethoxy-*p*-phenylene vinylene), PDMPV and poly(2,5-thienylene vinylene), PTV, using the precursor polymer methodology, and from polyaniline, PANI, using the method of processing as polyblends with poly-(*p*-phenylene terephthalamide), PPTA, from sulfuric acid. The solubility of both PANI and PPTA in H_2SO_4 presents a unique opportunity for co-dissolving and blending PANI and PPTA to exploit the excellent mechanical properties of PPTA and the electrical conductivity of PANI; we summarize the electrical and mechanical properties of such composite fibers. For PDMPV and PTV fibers, we find a strong correlation between the conductivity and the tensile strength (and/or modulus), and we show from basic theoretical concepts that this relationship is an intrinsic feature of conducting polymers.

I. INTRODUCTION

In conjugated polymers, the π-bonding leads to π-electron delocalization along the polymer chains and to the possibility of relatively high charge carrier mobility, μ, which is extended into three dimensional transport by the interchain electron transfer interactions.[1] The high density of redox sites within the π-electron system (essentially one per monomer) offers the additional advantage of a relatively high density, n, of carriers (charge e) through doping. Thus, high electrical conductivity, $\sigma = ne\mu$, is possible. As a result of the same intrachain π-bonding and relatively strong interchain electron transfer interactions, the mechanical properties (Young's modulus and tensile strength) of conjugated polymers are potentially superior to those of saturated polymers, such as polyolefins. Moreover, because of these two features, it may be possible to achieve exceptional mechanical properties with aligned conjugated polymers at lower chain lengths than required for their saturated

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counterparts.[2] Thus, conjugated polymers are of special interest because of the potential of a unique combination of electrical and mechanical properties.[3]

Since the electrical and mechanical properties are currently limited by defects and structural disorder, improvement in material quality that will enable the exploration of intrinsic properties has become an important goal of conducting polymer research.[3] It has been long recognized, however, that conjugated polymers tend to be insoluble and infusible. Thus, the question to be answered is whether or not processing methods can be developed that will lead to chain extended and chain aligned materials of sufficient quality. Significant progress has been made; the addition of long alkyl side chains[4] has opened opportunities for processing from solution or from the melt. However, the relatively bulky side chains decrease the π-electron density (and thus the carrier density) and the interchain coupling, thus making it more difficult to achieve the structural coherence needed to obtain high carrier mobility and exceptional mechanical properties.

A promising strategy to approach the intrinsic mechanical and electrical properties is through the use of the versatile precursor route which involves the preparation of a processible precursor polymer and subsequent conversion of the precursor polymer to the conjugated polymer.[5,6] The significant advantage of this route is that the saturated precursor polymers can be processed from solution prior to the thermal conversion to the conjugated final product. The precursor polymers may, therefore, be drawn prior to and during the thermal conversion process so as to yield oriented, homogeneous conjugated polymers.

Poly(*p*-phenylenevinylene), PPV, and its derivatives such as poly(dimethyl-*p*-phenylenevinylene) can be prepared from a precursor polymer, a polyelectrolyte, which is soluble in water.[6] The dimethoxyderivative of PPV, poly(2,5-dimethoxy-*p*-phenylene vinylene), PDMPV, has been prepared via a similar precursor route to PPV and exhibited high conductivities after doping. However, the commonly used aqueous solutions of the PDMPV precursor polymer tend to form gels, and the gradual elimination of the sulfonium group in the solid precursor cannot be avoided even at room temperature; both effects make subsequent processing into highly oriented films and fibers difficult. Recently, the Kyushu University group[7] succeeded in the preparation of dense PDMPV film from a new precursor polymer which is soluble in common organic solvents, easily processible, and stable even at 100°C. Similarly, poly(2,5-thienylene vinylene) (PTV) is one of the larger class of poly(arylenevinylene polymers which is attractive as a conjugated polymer and which can be synthesized via the precursor polymer route. As with PDMPV, the Kyushu University group[8,9] and Murase *et al.*[10] have found that PTV can be prepared through a new precursor polymer which is soluble in common organic solvents and chemically stable.

An alternative strategy is to identify stable conjugated polymer systems that can be processed. Of this class, polyaniline (PANI) is certainly a promising example. The use of concentrated acids[11] as solvents for PANI has specific advantages in that both the salt and the base form can be completely dissolved at room temperature, with polymer concentrations ranging from extremely dilute to more than 20% (w/w), in concentrated protonic acids such as H_2SO_4, CH_3SO_3H, and CF_3SO_3H. Perhaps more important is the fact when precipitated from acid solution, PANI comes out in the conducting (protonated) emeraldine salt form.[11] Although the ability to process conducting polyaniline from solution represents genuine progress, fibers and films made from these solutions have mechanical properties which are not adequate for many applications due mainly to the low molecular weight of the polyaniline used.[12] Fibers with significantly enhanced mechanical properties have been obtained by blend processing polyaniline with the rigid chain polymer poly-(*p*-phenylene terephthalamide), PPTA.[13] It is well known that PPTA is processed from solutions in concentrated H_2SO_4 to yield one of the strongest and stiffest fibers commercially available.[14] The process takes advantage of the fact that PPTA is a rod-like polymer that exhibits a liquid crystalline phase at high solution concentrations which facilitates the formation of highly oriented structures.[15]

In this review, we present a summary of our recent results on the electrical and mechanical properties of fibers made from PDMPV[16] and PTV[17] using the precursor polymer methodology, and from PANI using the method of processing as polyblends with PPTA from sulfuric acid.[13]

II. EXPERIMENTAL METHODS AND TECHNIQUES

A. Preparation of Precursor Polymers for PDMPV and PTV

The preparation of the precursor polymer and conversion to the conjugated polymer are summarized in Figure 1a (PDMPV) and 1b (PTV). Details on the synthesis of the precursor polymer and the conversion to the conjugated polymer are presented elsewhere.[16,17]

Differential scanning calorimetric (DSC) measurements of the polymer were carried out using a Mettler DSC 30, with the sample under nitrogen. The DSC thermogram of the PDMPV precursor polymer indicated a glass transition at 110°C, well-separated in temperature from the ≈195°C needed for thermal elimination of the methoxy leaving groups (Scheme 1a). For the PTV precursor polymer, the glass transition is at 50°C, again, well-separated in temperature from the elimination of methoxy leaving groups, which occurred at 188°C.

B. Preparation of the PANI/PPTA Blends[13]

The synthesis of the polyaniline used in this study was reported elsewhere.[8,9] Poly (*p*-phenylene terephthalamide) with inherent viscosity of 7.43 dl/g was obtained from Du Pont as Kevlar® powder.

A stock solution of 2 wt% PPTA in sulfuric acid was prepared by mixing 3.76 g of PPTA in 100 ml of 98% H_2SO_4 (Fisher). The mixture was mechanically stirred overnight to yield a homogeneous solution. This solution was also used to produce the 100% PPTA fibers. Polyaniline was weighed into a vial and concentrated H_2SO_4 was subsequently added. The mixture was stirred until the polyaniline dissolved and the solution was homogeneous. An amount of 2 wt% PPTA stock solution was added to yield a desired specific PANI/PPTA ratio. The mixture was mechanically stirred for 5 to 12 hours at room temperature, and then allowed to stand for 24 hours before spinning, to let the trapped air escape. In all cases, optically

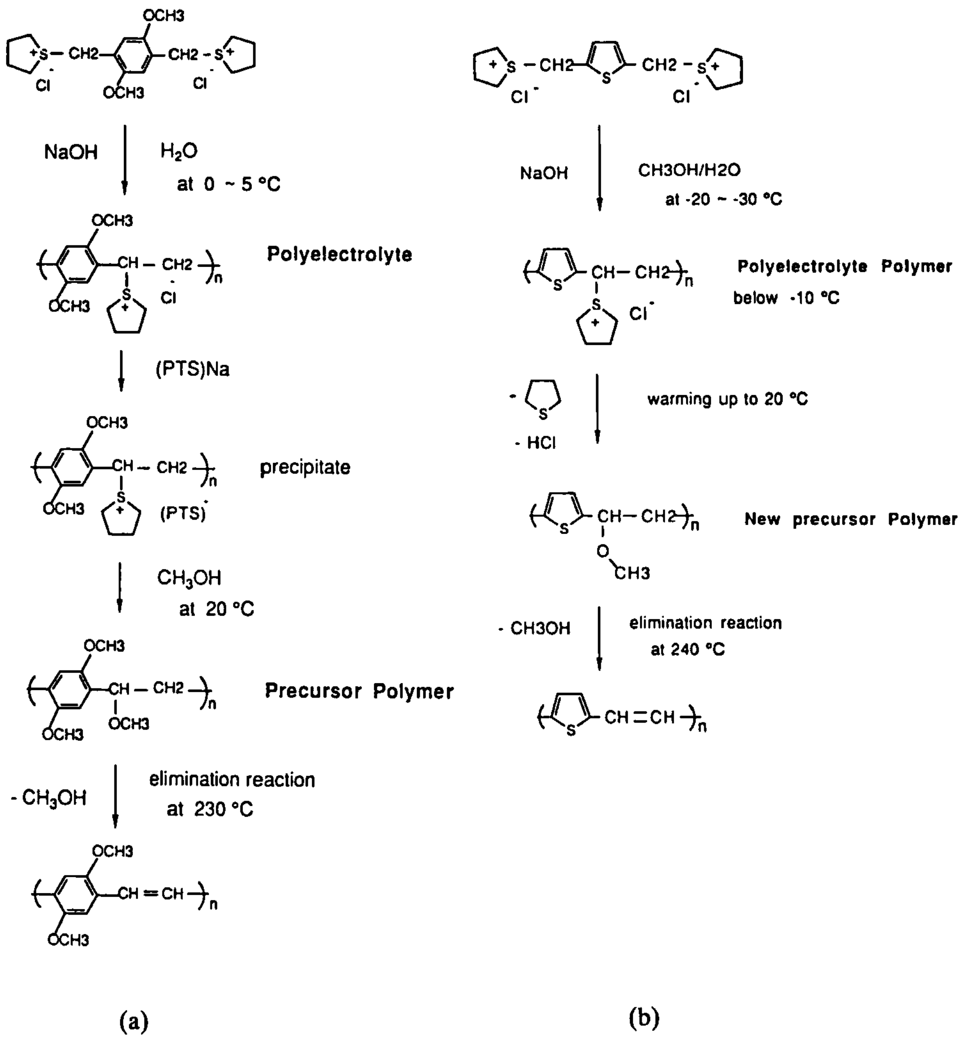

FIGURE 1 a: Synthesis of poly(2,5-dimethoxy-*p*-phenylenevinylene) from precursor polymer soluble in organic solvents. b: Synthesis of poly(2,5-thienylene vinylene) from precursor polymer soluble in organic solvents.

homogeneous solutions were obtained. Since the concentration of PPTA in the solutions was maintained at 1.5 wt% (which is below the onset of the formation of the lyotropic phase; typically at 6–8 wt% PPTA[11]), these polyblend fibers were spun from isotropic solutions.

C. Fiber Spinning, Drawing and Conversion of PDMPV[16] and PTV[17]

Details on the fiber spinning of the purified precursor polymers are given elsewhere.[16,17] For PDMPV and PTV, the precursor polymers were dissolved into chloroform. The solutions were spun using a high precision syringe pump (Sage

Instruments, model 355). The viscous solutions were pumped at a speed of 0.013 ml/min through a needle with diameter of 0.5 mm into hexane; the resulting precursor fibers were taken up onto a bobbin at a speed of 30 cm/min. The precursor polymers were dryed in a vacuum oven overnight; uniform pale yellow fibers were obtained with diameters of 50–100 μm. The drawing of the precursor fiber and conversion to fibers of the conjugated polymer were carried out using a temperature controlled, continuous drawing, tube furnace system.[16,17]

The PDMPV and PTV fibers were doped by exposure to the vapor pressure (approximately 1 mm Hg) of iodine at room temperature. Electrical measurements were carried out using the conventional four-probe method. The electrical conductivity was monitored *in-situ* during the doping; measurements were continued over a period of about an hour until the conductivity reached the steady state value.

D. PANI/PPTA Fiber Spinning[13]

The polymer blend solutions were wet spun into 1N H_2SO_4 using a high precision syringe pump. Monofilaments were collected onto a take-up spool; applied tension was applied to elongate the fiber during coagulation. The draw down ratio (take up speed/extrusion speed) invariably was as high as possible, for the production of continuous fibers; and it was increased from 7 to 20 with increasing PPTA concentration in the solution. Extrusion speed varied from 0.12 to 0.3 m/min and the windup speed from 1.8 to 4.2 m/min.

The fibers were prevented from drying on the bobbin by continually spraying them with deionized water; this procedure impeded the open structure of the wet spun fibers from collapsing and allowed removal of the residual H_2SO_4. Subsequently, the fibers were washed with running deionized water for 48 hr. Half of the bobbin was then submerged in 1.5N HCl for 12 hr. This allowed the acid to penetrate the fibers and homogeneously protonate them to the conducting emeraldine salt form (partial reduction of the emeraldine salt occurs during the washing; the HCl treatment restores PANI to the fully protonated form). Finally, the bobbin was placed in an oven and the fibers dried under vacuum at 50°C while maintained at constant length by the bobbin. The pure PPTA fibers were spun with the same method. The pure polyaniline solution was dry-jet wet spun into a 1N H_2SO_4 solution. Washing, HCl treatment, and drying was carried out as described for the blend fibers.

III. RESULTS

A. PANI/PPTA

Wide angle X-ray patterns of the composite fibers consisted of superimposed reflections from the two components, indicating that PANI and PPTA segregated during the coagulation.[13] In Figure 2 (inset), the conductivity vs volume fraction of PANI is shown on a log-log plot; the results indicate that over a relatively wide range of concentrations, the conductivity follows a simple power law,

$$\sigma = \sigma_0 f^{\alpha} \tag{1}$$

where f is the weight fraction of PANI. The solid curve in Figure 2 shows the power law fit to the experimental data with $\alpha = 7.9$ and $\sigma_o = 3.93 \times 10^{-14}$; the conductivity varies with fractional concentration of conducting polymer (from 10–70% PANI) according to Equation 1 over a range of values spanning nearly seven orders of magnitude.

In the context of percolation theory,[18] at sufficiently dilute concentrations such that there are no connected paths, the conductivity would be zero. As the concentration of conducting polymer is increased above the percolation threshold, the conductivity would become finite and increase as the connectivity (i.e. the number of conducting paths) increases. In contrast, the data presented in Figure 2 show no indication of a well-defined percolation threshold. Attempts to estimate a value for the percolation threshold (f_p) by fitting the data to the form $\sigma = \sigma_o(f-f_p)^\alpha$ lead to the conclusion that f_p is below $\cong$1%. By contrast, classical percolation theory for a three-dimensional network of conducting polymer globular aggregates in an insulating matrix predicts a percolation threshold at a volume fraction $f_p \approx 0.16$.[18] Percolation at $f_p \approx 0.16$ has been observed for conducting polymer composites.[19]

On the other hand, for rod-like structures with length L and diameter d (e.g. a more fibrillar conducting network), the percolation threshold is determined by the excluded volume per fibril ($\approx \pi L^2 d$).[20] With N fibrils per unit volume, the percolation threshold is given by $f_p \approx N\pi L^2 d = N\pi L d^2(L/d) = f_{fib}(L/d)$ where f_{fib} is the

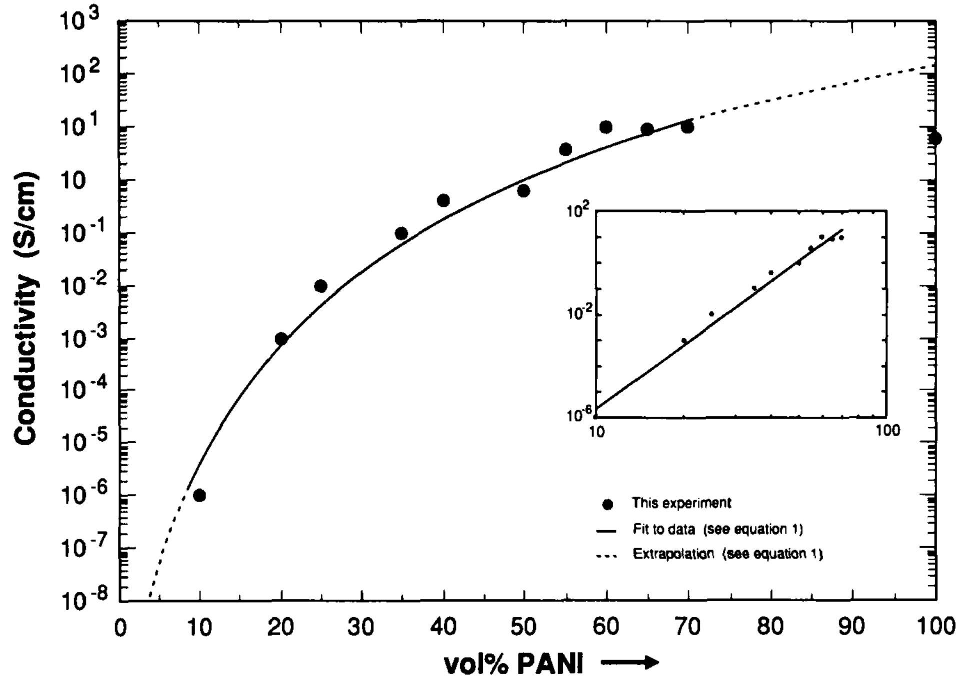

FIGURE 2 Conductivity versus volume fraction of PANI in the fiber; the inset shows the same data on a log-log plot.

volume fraction of conducting material in the fibrillar network. Thus, the onset of conductivity would occur at $f_{\text{fib}} = f_p(d/L) << f_p$. The analogous percolation of molecularly dispersed rods was observed[21] for polydiacetylene in solution in toluene, where the onset of gelation (i.e. the formation of a connected mechanical network) occurs at a volume fraction of only 0.04%. Since PPTA precipitates from sulfuric acid at a lower water content (at ≅10 wt%) than PANi (at ≅25 wt%), the PPTA comes out of solution first and forms a mechanically connected network. That structure may serve to assemble the conducting PANI along the pre-existing connected paths, thereby leading to the kind of fibrillar conducting pathways that would decrease the percolation threshold to $f_p << 0.16$.

B. PTV[17]

The Young's modulus and the tensile strength of the PTV fibers were measured at room temperature. Figure 3 shows the Young's modulus plotted against draw ratio; Figure 4 displays the tensile strength plotted against draw ratio. The modulus of the undrawn, converted PTV fiber was 1.1 GPa. Values of the Young's modulus of 7 GPa and of the tensile strength of 0.5 GPa were obtained for fibers which had been drawn to 20 times their initial length.

The tensile strength of 0.5 GPa is identical to the value as reported for highly stretched PPV film prepared by a heated roll method[22] and comparable to the values obtained with stretched *trans*-polyacetylene films.[23] The modulus, however, was lower than the values reported for stretched PPV films[22] and for stretched polyacetylene[23] films.

The conductivities of the iodine-doped PTV fibers were measured at room temperature. The conductivity rapidly increased after the PTV fibers were exposed on iodine vapor, approaching maximum values after about 1 hour. Figure 5 shows the conductivity plotted against the draw ratio. The undrawn PTV fiber exhibited a conductivity of 80 S/cm. As expected, the conductivity was found to increase with the draw ratio; the maximum conductivity of 2000 S/cm was obtained at the max-

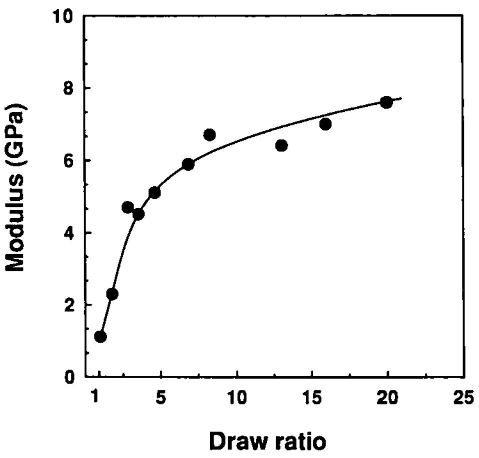

FIGURE 3 Relationship between draw ratio and modulus of PTV fibers.

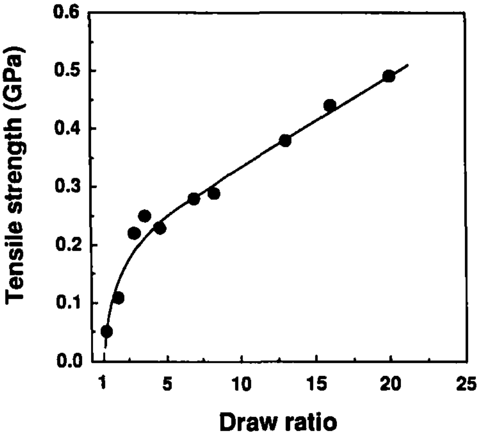

FIGURE 4 Relationship between draw ratio and tensile strength of PTV fibers.

imum draw ratio. This value was 20 times higher than that of an undrawn fiber and comparable to that of an oriented film reported by Murase *et al.*[10] The relationship between the conductivity and the draw ratio was similar to that for the modulus and tensile strength (and draw ratio), indicating a strong correlation between conductivity and the mechanical properties.

This correlation between the structural dependence (as induced by the draw ratio) of the mechanical and electrical properties are illustrated more clearly by Figures 6 and 7, where the conductivity of drawn/converted PTV samples is plotted against, respectively, the modulus and the tensile strength. In both cases, an essentially linear relationship is found.

The many complex molecular processes that simultaneously occur in the drawing/conversion process need to be carefully optimized so that their time scales are in harmony. The critical parameters for process optimization are the degree of preconversion, deformation rate, process-temperature profile, conversion-catalyst

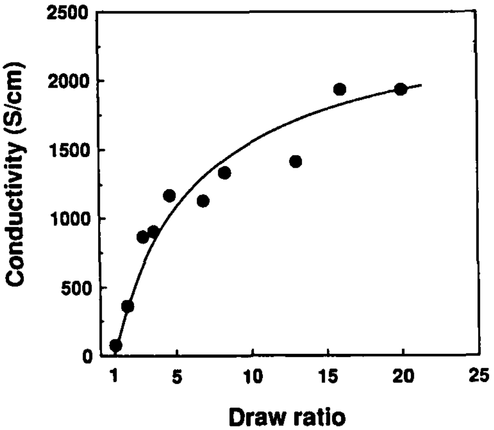

FIGURE 5 Relationship between draw ratio and conductivity of PTV fibers.

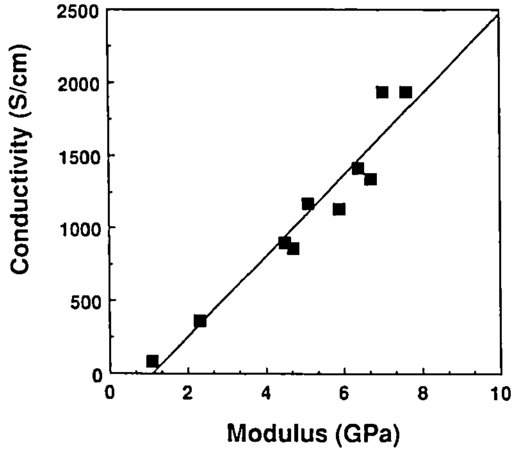

FIGURE 6 Correlation between modulus and conductivity of PTV fibers.

concentration, and residence time. Obviously, in this initial study of PTV, we have not developed a fully balanced set of processing parameters. This is illustrated by the modest orientation indicated by the X-ray patterns.[16] Nevertheless, the current materials have a Young's modulus of 7 GPa, a tenacity of 0.5 GPa and a conductivity of 2000 S/cm; a combination of properties which are adequate for conductive textile applications. It should be clear that further optimization of the inter-related processing variables will undoubtedly result in materials of superior quality.

C. PDMPV[16]

The Young's modulus and the tensile strength of PDMPV fibers are shown versus draw ratio in Figures 8 and 9. The undrawn PDMPV fiber exhibited relatively poor

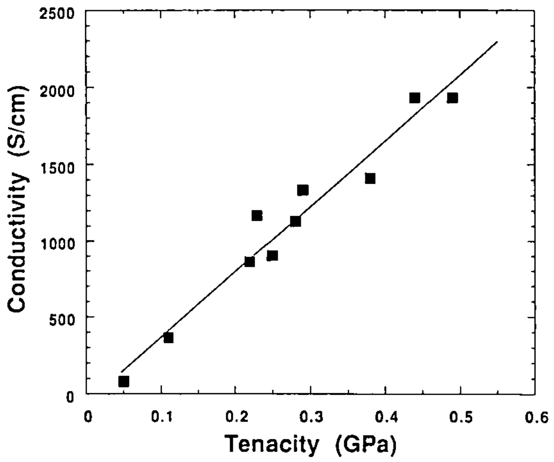

FIGURE 7 Correlation between tensile strength and conductivity for PTV fibers.

mechanical properties: the modulus and tensile strengths were 1.3 GPa and 0.07 GPa, respectively. Figures 8 and 9 reveal that fibers which had been drawn to 8 times their initial length had a Young's modulus as high as 35 GPa and a tensile strength of 0.7 GPa. The effects of doping on the mechanical strength are also displayed (filled circles in Figures 8 and 9). The data presented on these graphs indicate that doping caused only a moderate reduction of modulus and essentially no loss of tensile strength.

Figure 10 shows the conductivity plotted against draw ratio. The undrawn PDMPV fiber exhibited a conductivity of 20 S/cm, with a gradual increase of conductivity seen up to a draw ratio of 5. At draw ratios greater than 5, the conductivity increased dramatically, as reported for stretched films[15] (although different in detail, since

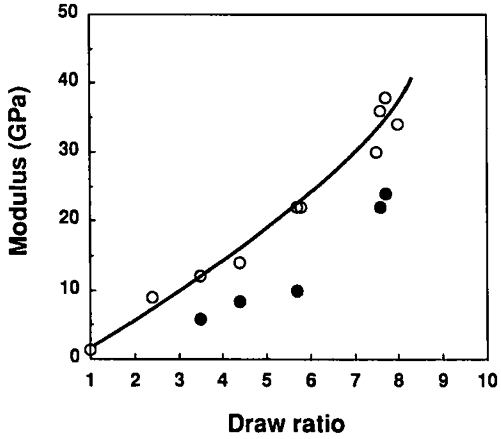

FIGURE 8 Young's modulus as a function of the draw ratio for PDMPV fiber (open circles) and for PDMPV fiber doped with iodine (closed circles).

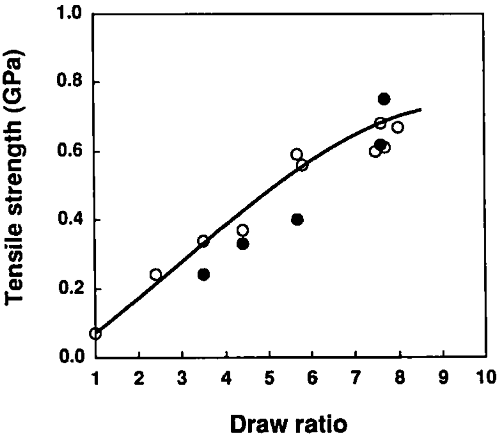

FIGURE 9 Tensile strengths as a function of the draw ratio for PDMPV fiber (open circles) and for PDMPV fiber doped with iodine (closed circles).

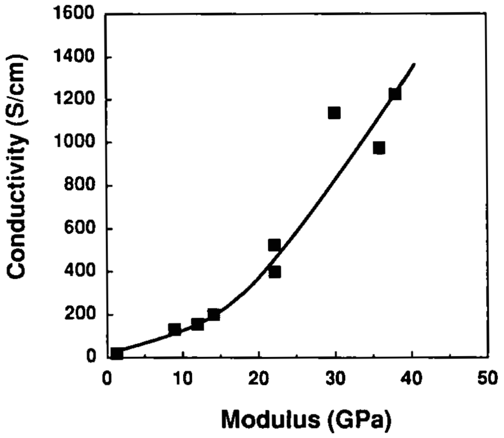

FIGURE 10 Electrical conductivity as a function of the draw ratio of PDMPV fiber.

in Reference 15 the unstretched films were already about 30% converted). At a draw ratio of 8, the conductivity was 1200 S/cm, 60 times higher than that of the undrawn material.

Figures 11 and 12 show the relationship between Young's modulus and electrical conductivity (Figure 11) and between the tensile strength and electrical conductivity (Figure 12) for drawn PDMPV fibers. In both cases, a strong correlation is observed.

IV. DISCUSSION

Although the electrical conductivity of conducting polymers is enabled by intrachain transport, in order to avoid the localization inherent to one-dimensional

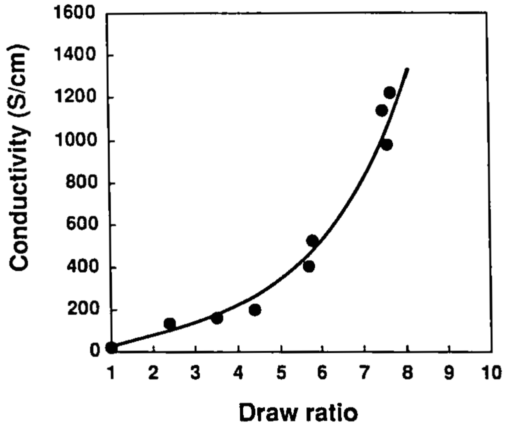

FIGURE 11 Electrical conductivity as a function of Young's modulus for PDMPV fiber.

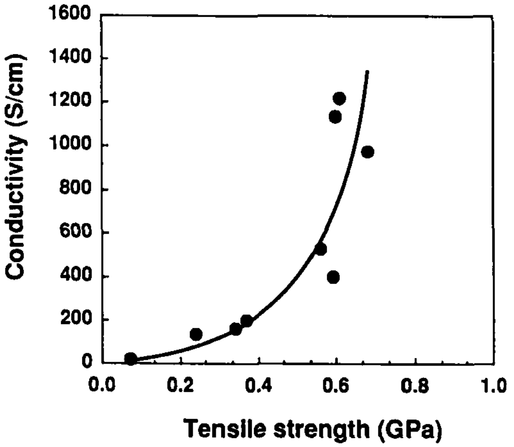

FIGURE 12 Electrical conductivity as a function of the tensile strength for PDMPV fiber.

systems, one must have the possibility of interchain charge transfer.[1,3] The electrical transport becomes essentially three-dimensional (and thereby truly metallic) so long as there is a high probability that an electron will have diffused to a neighboring chain between defects on a single chain. For well-ordered crystalline material in which the chains have precise phase order, the interchain diffusion is a coherent process. In this case, the condition for extended transport is that[1,3]

$$L/a >> (t_o/t_{3d}) \tag{2}$$

where L is the coherence length, a is the chain repeat unit length, t_o is the intrachain π-electron transfer integral, and t_{3d} is the inter-chain π-electron transfer integral. An analogous argument can be constructed for achieving the intrinsic strength of a polymer. If E_o is the energy required to break the covalent main-chain bond and E_{3d} is the weaker interchain bounding energy (from Van der Waals forces and hydrogen bonding for saturated polymers), then the requirement is coherence over a length L such that[2,3]

$$L/a >> E_o/E_{3d}. \tag{3}$$

In this limit the large number (L/a) of weak interchain bonds add coherently such that the polymer fails by breaking the covalent bond. The direct analogy between equations 2 and 3 is clearly evident. In fact, for conjugated polymers, E_o results from a combination of σ and π bonds (the latter being equal to t_o, see Equation 2) and E_{3d} is dominated by the interchain transfer integral, t_{3d}. Thus, Equations 2 and 3 predict that quite generally the conductivity and the mechanical properties will improve in a correlated manner as the degree of chain alignment is increased, with each approaching intrinsic values when the inequalities of Equations 2 and 3 are satisfied. These predictions are in general agreement with the data obtained from PTV and PDMPV as shown in Figures 6, 7, 11, and 12. In both PTV and

PDMPV, a strong correlation is observed, suggesting that major improvements in electrical conductivity can be anticipated as the materials are further improved such that the mechanical properties approach their intrinsic values. However, until a more quantitative understanding of the implied relationships is attained, extrapolation to the intrinsic electrical conductivity is not possible.

V. CONCLUSIONS

We have demonstrated that blend fibers of polyaniline and poly (*p*-phenylene terephthalamide) can be derived from solutions in concentrated sulfuric acid. A minor amount of PPTA significantly improved the mechanical properties of PANI fibers while retaining the conductivity of pure polyaniline. These results indicate, therefore, that processing PANI/PPTA from concentrated sulfuric acid represents a viable method for producing polyblend fibers with mechanical properties in the textile range and with moderate levels of electrical conductivity. In this study, the concentration of PPTA was below the onset of the formation of the lyotropic phase; we anticipate that results obtained with lyotropic systems will exhibit improved properties.

Oriented PDMPV fibers exhibited excellent mechanical properties (modulus and strength were 35 GPa and 0.7 GPa, respectively) and high electrical conductivity ($\sigma \approx 1200$ S/cm after iodine doping). The mechanical properties were retained after doping; the modulus only decreased to 25 GPa, and the tensile strength remained essentially unchanged. In the case of PTV, orientation of fibers resulted in both improved mechanical properties and high conductivity; the current materials have a Young's modulus of 7 GPa, a tenacity of 0.5 GPa and a conductivity of 2000 S/cm.

We have shown that the modulus and tensile strength derive from a combination of the intra-chain interactions (e.g. strength of chemical bonding, chain conformation, etc.) and inter-chain interaction (e.g. van der Waals forces, interchain transfer interactions, chain conformation, etc.). In conjugated polymers, these same features (band conduction within a polymer chain and efficient electron transfer between polymer chains) determine the carrier mean free path, and thus, the electrical conductivity. Therefore, we conclude that the mechanical and electrical properties of conjugated polymers are intrinsically linked, and we anticipate that in general as the tensile strength (and/or modulus) improve with improved chain orientation, the electrical conductivity will show corresponding improvements until both approach their respective intrinsic theoretical values.

Acknowledgment

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