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Thermal Process for Orientation of Polyaniline Films

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ABSTRACT: It is demonstrated that films of the emeraldine base form of polyaniline can be processed through simultaneous heat treatment and application of stress to produce oriented, partially crystalline polyaniline films. The emeraldine base films were produced by casting emeraldine base polymer dissolved in NMP (*N*-methylpyrrolidinone) onto smooth glass substrates. The resulting films contained up to 20% by weight NMP. Heating the samples at an elevated temperature ($T \gtrsim 110$ °C) while under stress leads to an elongation of the polymer film with l/l_0 up to 4.5. The resulting material has enhanced mechanical properties with tensile strengths of the emeraldine base films increasing from an average of 54 MPa for unstretched films to an average of 124 MPa for 4-fold uniaxially stretched films. A 2× biaxially stretched polyaniline film has a tensile strength similar to that of a 4× uniaxially stretched film. The X-ray diffraction studies show a directional enhancement of the Debye-Scherrer rings, indicating a spreading angle of ~7°, reflecting significant orientation of the polymer chains. Similarly, infrared and UV visible spectroscopy reveal anisotropic optical constants. Detailed analysis of the infrared spectra gives a measure of the angle between the phenyl rings and the plane defined by the nitrogens of the polyaniline backbone. Temperature-dependent audio-frequency conductivity studies of oriented emeraldine base show anisotropy in the normalized conductivity with $\sigma_\parallel/\sigma_\perp \sim 3$ in accord with hopping conductivity in the anisotropic undoped emeraldine base. In contrast, the dc conductivity of oriented emeraldine hydrochloride salt shows a 10-fold increase in dc conductivity for $\sigma_\parallel$ as compared with unoriented material, with $\sigma_\parallel/\sigma_\perp \sim 3.5$. Both $\sigma_\parallel$ and $\sigma_\perp$ vary as $\exp[-(T_0/T)^{1/2}]$ with $T_{0\parallel} \sim 5500$ K and $T_{0\perp} \sim 6500$ K, indicating that the dc conductivity is dominated by quasi-one-dimensional variable-range hopping in the amorphous regions between the crystalline areas.

I. Introduction

The ability to process electronic polymers into tough, free-standing films has been an important achievement during the past decade. Although it is possible to stretch-orient *cis*-polyacetylene and subsequently dope it to form highly conducting doped *trans*-polyacetylene, these materials are generally not stable in air.[1-4] Recently, it was shown that electrochemically prepared conducting polypyrrole films can be oriented via stretching, producing up to a 2-fold elongation and a concomitant increase in conductivity.[5,6]

The polyaniline family of polymers is a particularly versatile system. The fully reduced leucoemeraldine base polymer, the fully oxidized pernigraniline base polymer, and the intermediate oxidation level emeraldine base polymer (Figure 1) are all insulators. Protonation of emeraldine base, oxidation of leucoemeraldine base, and reduction of pernigraniline base result in formation of the conducting emeraldine salt polymer (Figure 1d).[7] It has previously been shown that powders of emeraldine salt are up to 50% crystalline.[8] Both the insulating emeraldine base and the conducting emeraldine salt are stable in air though the degree of oxidation of the emeraldine base is dependent upon whether it is prepared in air or in inert atmosphere.[7,9] Emeraldine base is soluble in *N*-methylpyrrolidinone (NMP)[10-12] as well as in sulfuric acid[13-15] 80% aqueous acetic acid, and 60-88% aqueous formic acid.[16] Strong lustrous flexible films can be obtained from solutions of NMP.[11] Recently, it has been reported that fibers can be drawn of both the emeraldine base[17] and emeraldine salt polymers.[15]

In this paper, we present an initial study of the thermal processing for orientation of the emeraldine base polymer.[18,19] Films of emeraldine base polymer are cast from NMP. These films contain up to 20% by weight NMP, which acts as a plasticizer, lowering the glass transition temperature, T_g.[20] Heating of these samples to temperatures above T_g ($T \gtrsim 110$ °C for films with 20% by weight NMP) while maintaining the sample under a uniaxial stress results in up to 450% elongation ($l/l_0 = 4.5$) and concomitant polymer chain orientation as confirmed by X-ray diffraction, polarized infrared and UV/vis spectroscopy, and conductivity studies. Initial studies show that upon uniaxial and biaxial orientation of the polymer the tensile strength increases substantially to values comparable to those of commercially available polymer materials.

II. Experimental Section

Emeraldine salt was synthesized in air or inert atmosphere by the oxidative polymerization of aniline in aqueous HCl using ammonium peroxidisulfate $(NH_4)_2S_2O_8$, as the oxidizing agent.[21] The resulting material is partly crystalline and classified as ES-I.[8] This polymer was then deprotonated by 0.1 M aqueous ammonium hydroxide to give an amorphous emeraldine base

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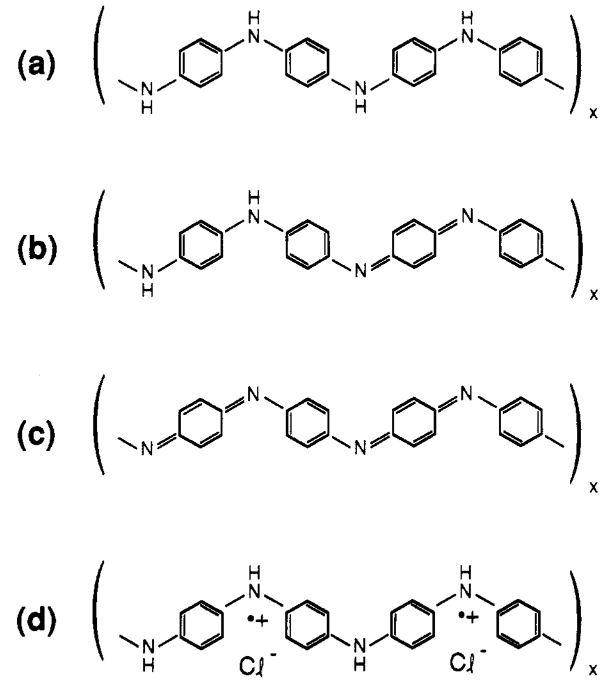

Figure 1. Oxidation states of polyaniline[7] characterized by the fraction $1 - y$ of oxidized and y of reduced repeat units: (a) leucoemeraldine base ($1 - y = 0$); (b) emeraldine base ($1 - y = 0.5$); (c) pernigraniline base ($1 - y = 1$); and (d) emeraldine salt polymer.

powder, classified as EB-I. The emeraldine base powder is soluble in NMP. Films of EB-II were made from a 2% solution (w/w) of emeraldine base in NMP made by slowly adding 20 g of finely ground emeraldine base powder to 1 L of constantly stirred NMP. Approximately 250 mL of this solution was poured onto a clean 23 cm × 38 cm sheet of glass. Two of these coated glass sheets were placed in a vacuum oven (Fisher Isotemp) at ~50 °C for ~24 h. The films were removed from the glass by immersion in distilled water. These films, which are flexible and copper colored, may be partially crystalline and are 10–50 μm thick. Chemical analysis is in excellent agreement with the emeraldine base structure. Samples of oriented emeraldine salt (ES-II) were obtained by equilibrating the oriented EB-II with HCl of pH = 0.0.

X-ray diffraction studies were carried out using the photographic detection method with a sealed-tube Cu Kα source. Densitometer tracings of the exposed films were obtained by a Joyce-Loeble densitometer. Infrared transmission spectra were measured with a Nicolet 60 SX spectrometer using a wire grid polarizer. Optical spectra were recorded by a PTI 01-001 monochromator and polymer film polarizers. Audio-frequency conductivity measurements were carried out using a General Radio 1621 precision capacitance bridge and a Delta Design Model 5900 cryogenic oven. dc conductivity studies utilized a Keithley Model 220 current source and Model 181 nanovoltmeter together with a CTI Cryotronics closed-cycle temperature-control system. Thermal processing of the polymer was carried out in the Delta Design Model 5900 cyrogenic oven under inert gas with known tensile stress applied to the polymer. Other uniaxial and biaxial orientation studies were carried out in the laboratories of Foster-Miller, Inc., in Waltham, MA. For this work the films were cut into strips 3.8 cm wide by 38 cm long. Each strip was threaded through a uniaxial web stretching device[22] where it contacts two heated rollers. Stretching takes place at the first roller, which is set at 148 ± 2 °C. The second roller is used for annealing the sample and is set at 95 ± 2 °C. Stretching ratios are controlled by varying the speeds of the pinch rollers as the film is fed through the device.

III. Results and Discussion

In typical experiments, the sample of emeraldine base was maintained under a stress of approximately 2×10^7 N/m^2. The sample length increases slightly with temperature with a thermal expansion coefficient α of approximately 0.4×10^{-4} K^{-1} for temperatures between −150 and 0 °C as compared to the value of 0.8×10^{-4} K^{-1} for Nylon 6 and $(1.0–2.0) \times 10^{-4}$ K^{-1} for polyethylene.[23] Between 0 and 60 °C the sample length is nearly independent of temperature. Upon increasing the temperature beyond 60 °C, there is a continuous increase of sample length with a rapid increase above 110 °C. Samples of emeraldine base with differing NMP contents show a minimum temperature for elongation that decreases with increasing NMP content. This is in accord with the results of dynamic mechanical testing, which indicates the presence of a glass transition in the range of 110–150 °C for emeraldine base dependent upon the NMP content.[20,24] The maximum elongation obtained before break was 450%.

Table I
Tensile Strength of Polyaniline Films

material	tensile strength,[a] MPa
NMP-cast emeraldine base film[b]	54.4
uniaxially stretched (4×) emeraldine base film[b]	124
biaxially stretched (2× by 2×) emeraldine base film[b]	122

[a] Gauge length: 7.5 cm. [b] Contains ~15% NMP plasticizer.

The tensile strength at low loads and the modulus at break were measured. The results, summarized in Table I, reveal that there is a substantial increase in the tensile strength for emeraldine base along the chain direction as a function of orientation. Biaxial orientation produces film with increased tensile strength in both stretch directions. For comparison, Nylon 6 films have a typical tensile strength of 62–83 MPa.[23]

X-ray diffraction studies of the stretched films demonstrate their microscopic orientation. Figure 2 shows photographs of the diffraction pattern for 4-fold elongated ($l/l_0 = 4$) EB-II and 4-fold elongated ES-II. A significant directional enhancement of the Debye-Scherrer rings is seen for stretched films. The coherence lengths of the crystalline regions of EB-II stretched films are approximately 150 Å parallel to the stretch direction and about 50 Å perpendicular to the chains. These coherence lengths are determined from the width of the X-ray diffraction rings using the Scherrer formula. From the angular fwhm of the scattering intensity, it is estimated that the spreading angle for the chains is ~±7°. The doped samples have a reduced orientation.

Infrared spectroscopy provides another convenient means to evaluate the chain orientation. Parts a and b of Figure 3 show the IR spectra of 4-fold stretched emeraldine base for light polarized parallel and perpendicular to the orientation direction. The major modes are identified at 820, 1150, 1300, 1500, and 1600 cm^{-1}. Figure 4 shows the dichroic ratio for the 820- and 1150-cm^{-1} modes as a function of the stretching ratio. The dichroic ratio is the ratio of the integrated oscillator strength for each mode in the parallel and perpendicular polarizations, $D \equiv I_\parallel/I_\perp$. Analysis of the dichroic ratio data is based on the assumptions that (1) all the rings are equivalent, (2) the 820-cm^{-1} mode is polarized perpendicular to the C_6 ring plane; (3) the 1150-cm^{-1} mode is polarized parallel to the N–N (zigzag) direction; and (4) the C–N–C angle in EB-II films is equal to 131°.[8,25] Analysis[26] of Figure 4 gives an estimate that the plane of the C_6 rings makes an angle of 56° ± 15° with respect to the plane of the nitrogen atoms, which is in reasonable agreement with the ring torsion angle of ~30° determined by analysis of X-ray diffraction patterns of the emeraldine base.

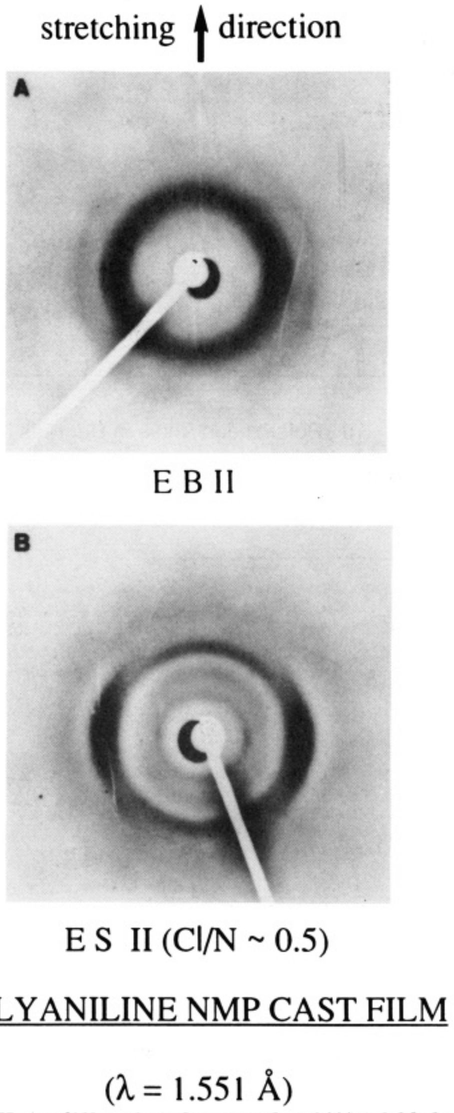

Figure 2. X-ray diffraction photographs of (A) 4-fold elongated EB-II and (B) ES-II derived by equilibrating the elongated EB-II with HCl at pH = 0 ([Cl]/[N] = 0.5). The X-ray wavelength utilized was 1.551 Å (from ref 25).

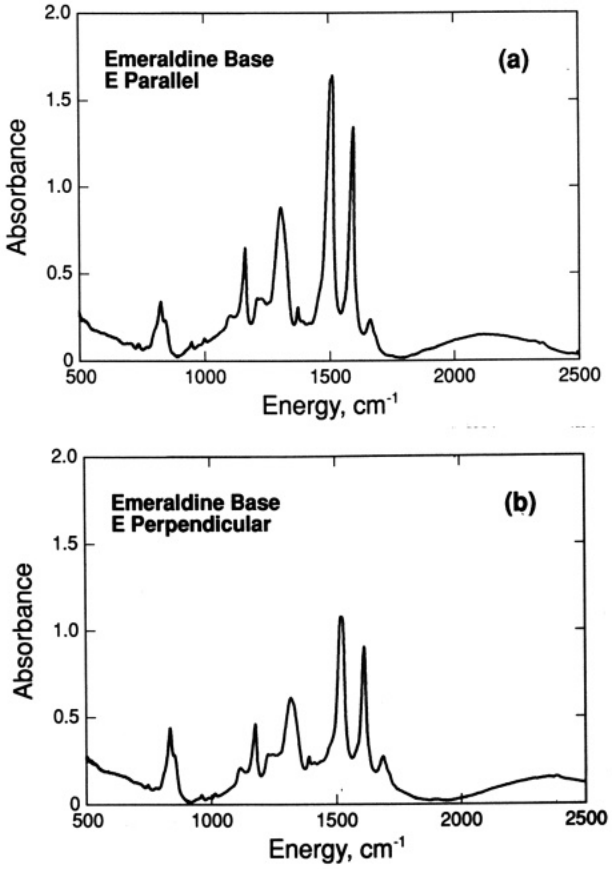

Figure 3. IR spectra for 4-fold stretched emeraldine base for (a) light polarized parallel and (b) light polarized perpendicular to the orientation direction.

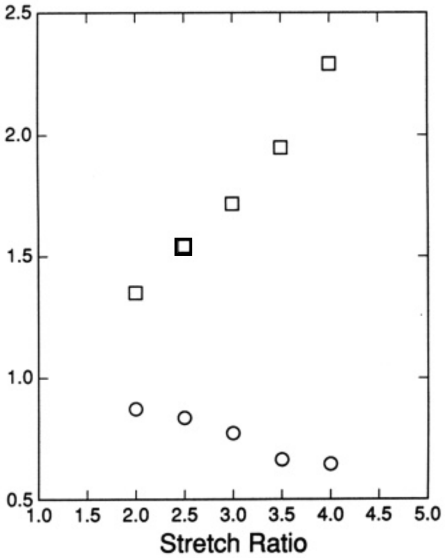

Figure 4. Dichroic ratio, $D \equiv I_{\parallel}/I_{\perp}$, for the 820 cm^{-1} (○) and 1150 cm^{-1} (□) IR modes as a function of the stretch ratio.

Figure 5 shows the dc conductivity as a function of temperature and direction for 4-fold elongated ES-II film. The conductivity parallel to the stretching direction is approximately 3 times larger than that perpendicular to the stretching direction with very similar but not identical temperature dependences, $\sigma_{\parallel,\perp}(T) \propto \exp[-(T_{0\parallel,\perp}/T)^{1/2}]$. $T_{0\parallel}$ is found to be 5500 K while $T_{0\perp}$ is 6500 K. Hence, the dc conductivity remains dominated by quasi-one-dimensional variable-range hopping in the amorphous regions. Dielectric constant and thermopower studies of the protonated stretched samples suggest that there is substantial three-dimensional delocalization within the crystalline regions.[27]

Similarly, parts a and b of Figure 6 show, respectively, the audio-frequency (10–10^5 Hz) conductivity for the perpendicular and parallel directions of EB-II oriented films for 78 K $\leq T \leq$ 311 K. The data are nearly indistinguishable with that obtained earlier for unoriented EB-I.[28] Comparison of these results with the previous analyses[28,29] suggests that the charge transport in the undoped polymer can be described by a modified variable-range hopping, with hops perpendicular to the chain more difficult than hops parallel to the chain. In other words, it appears as if the average hopping distance or hopping probability along the chain is larger than the hopping distance or hopping probability perpendicular to the chain.

Figure 7 is the polarization dependence of the reflectance at 730 nm (1.7 eV, the energy corresponding to the tail of the "excitonic" transition from the HOMO on the benzenoid to a LUMO on the quinoid[30,31]) of a 4-fold stretched EB-II film. It exhibits $\cos^2\theta$ behavior (where θ is the angle of polarization with respect to the stretching direction) as expected for an anisotropic absorption feature. However, for light polarized perpendicular to the chain direction, the reflectance is nonzero. The presence

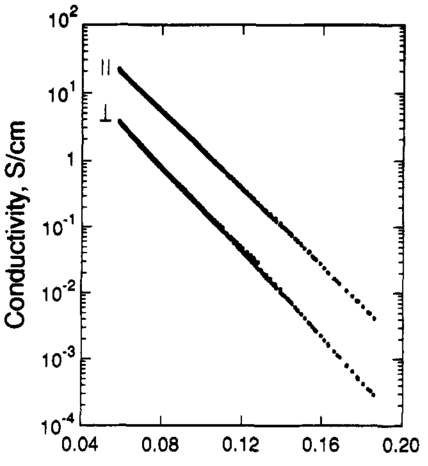

Figure 5. Temperature dependence of dc conductivity for pH = −0.25 equilibrated 4-fold elongated emeraldine film. The upper curve is for conductivity parallel to the stretch direction; the lower curve is for conductivity perpendicular to the stretch direction.

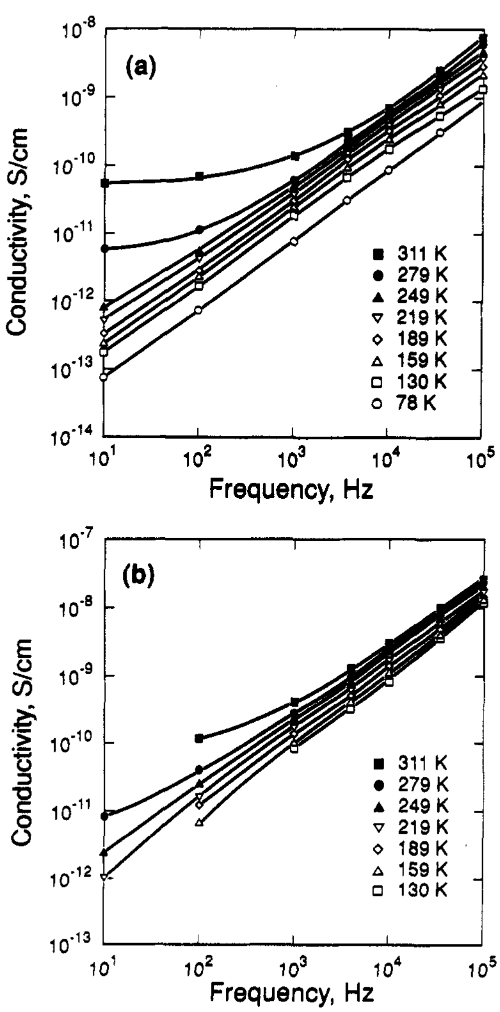

Figure 6. Frequency and temperature dependence of conductivity for 4-fold stretched EB-II: (a) perpendicular to stretch direction and (b) parallel to stretch direction.

of reflectance for perpendicularly polarized light may be caused by the zigzag nature of the emeraldine base chain such that the active chromophore has a component perpendicular to the chain axis as well as incomplete orientation of the polymer chains in the sample.

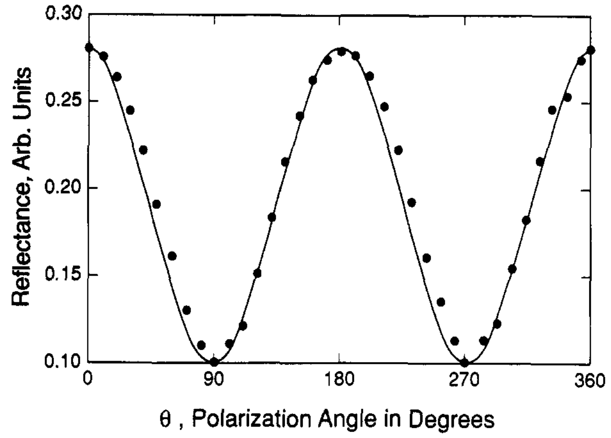

Figure 7. Polarization dependence of reflectance at 730 nm (1.7 eV) from a 4-fold stretched EB-II film (●). The solid curve is a fit to $\cos^2 \theta$ behavior.

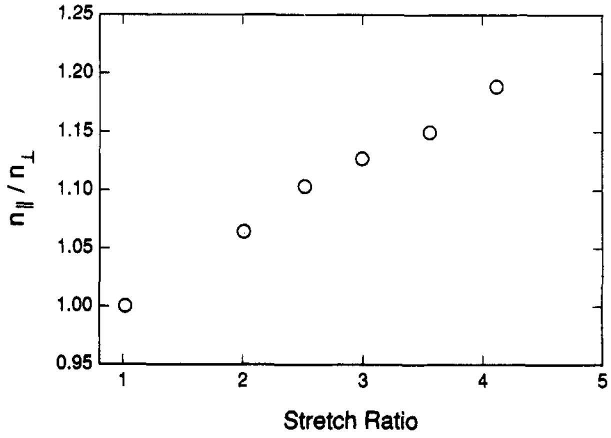

Figure 8. Variation of the ratio of the index of refraction in the near infrared for light polarized parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the stretch direction as a function of the stretch ratio.

The near-infrared absorption spectra in the parallel and perpendicular directions show a series of oscillations due to multiple internal reflections within the films. From the measured fringe periods and film thickness the near-infrared indices of refraction are calculated to be anisotropic with $n_{\parallel,3.5} = 1.82$ and $n_{\perp,3.5} = 1.58$ and $n_{\parallel,4.0} = 1.87$ and $n_{\perp,4.0} = 1.57$, where the subscript represents the stretching ratio. Figure 8 summarizes the variation of $n_{\parallel}/n_{\perp}$ obtained with stretch ratio.

Figure 9 shows the UV/visible reflectance for light polarized parallel and perpendicular to the stretch direction of a 4-fold stretched sample treated with HCl to form emeraldine salt. Though anisotropic, it is noted that there is considerable oscillator strength in the perpendicular as well as parallel directions. This again likely reflects the zigzag nature of the polymer chain and perhaps some contributions due to three-dimensional interactions between the chains as well as incomplete orientation of polymer chains. It is noted that the maximum in reflectance corresponds to the peak in energy of the metallic polaron band absorption.[32]

IV. Conclusion

We have demonstrated that emeraldine base polymer films can be processed to form strong oriented materials by maintaining the polymer under stress while the temperature is raised toward the glass transition temperature. After the orientation process, the polymer chains are significantly oriented parallel to the stretching direction. These stretch-oriented materials can then be treated

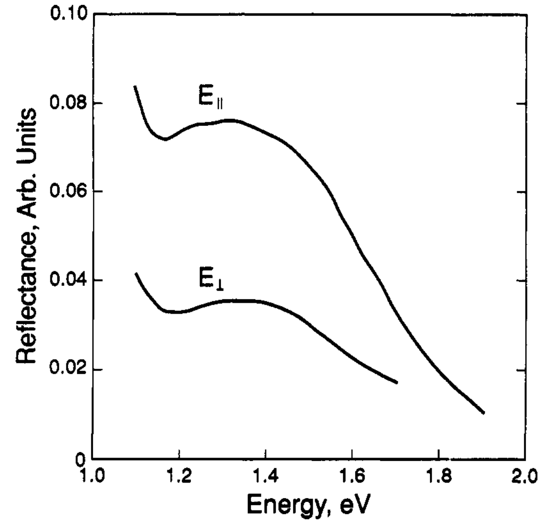

Figure 9. UV/visible reflectance for light polarized parallel and perpendicular to the stretch direction of 4-fold stretched l/l_0 = 4 film equilibrated with HCl to form ES-II.

with protonic acids to form emeraldine salt. These salt polymers are oriented to a lesser degree than the starting emeraldine base form. The oriented emeraldine base and emeraldine salt polymers show enhanced optical and electrical properties.

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