Shear-Induced Delocalization of Polarons in Polyaniline−Surfactant Complexes

Hanaa Khalil and Kalle Levon*

Polymer Research Institute, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201

Received January 29, 2002; Revised Manuscript Received July 10, 2002

ABSTRACT: A transition for a random coil to an extended chain conformation in dilute polyaniline solutions has been shown to induce delocalization of polarons and to increase the conductivity in the solid state by MacDiarmid et al. We have investigated a similar chain extension during a transition from isotropic to a liquid crystalline phase of polyaniline (PANi). We now report the use of an extra additive, the zinc salt of the dopant, to improve the viscoelastic behavior of the doped PANi complex by applying external force, shearing for the possibility of chain alignment. PANi was initially doped with dinonylnaphthalenesulfonic acid (DNNSAH), and then controlled amounts of the zinc salt of DNNSAH were added to this doped PANi complex in the solution state. The addition of zinc salt improved the viscoelastic behavior, and we were able to apply manual shear to the solid samples at elevated temperatures. The shearing was shown to induce chain alignment as seen by strong birefringence under the optical microscope and with the layered structure defined by X-ray diffraction experiments at room temperature in the cooled samples only after the shearing of the samples. The delocalization of polarons with free carrier tail extending to the near-infrared (NIR) was observed by UV−NIR spectroscopy to confirm the observed chain extension under the presented conditions. The electrical conductivity increased 3 orders of magnitude after the shear.

Introduction

MacDiarmid et. al. have shown that the delocalization of polarons in polyaniline (PANi) occurs due to the transition from coillike structures to extended chains with a concomitant reduction in π-defects caused by ring twisting.[1−3] In the dilute PANi solutions, this transition was achieved by the control of solvent quality, and the chain extension was confirmed with viscosity experiments. It was also concluded that the conductivities of the solid samples were higher in the samples obtained from the solutions in which PANi showed chain expansion than from the solvents in which PANi exhibited random coillike conformation. Although the phenomenon was named “secondary doping”, it is obvious that the phenomenon can be explained by the principles of dilute macromolecular solutions and represents a primary feature of the doped macromolecular chains.

In an interesting connection to this transition, Fredrickson has predicted chain extension with the increase in the surfactant concentration, when a surfactant interacts with a random coil.[4] The connection is relevant, as PANi is doped with surfactant-type acids due to the molecular characteristics of PANi. This inherently conducting polymer has attracted considerable attention because of its ease of preparation and environmental stability.[5−7] Strong intermolecular interactions between the stiff PANi backbone chains led to a polymer with high glass transition temperature and limited processing properties.[8] The use of counterion dopants has improved the processability[9] and has opened up new possibilities for the preparation of a variety of conductive polymer blends, either from solution[10] or from the melt state.[11] The counterions not only have the function of doping but also act as surfactants and thus improve the solubility and processing properties.[12] Dodecylbenzenesulfonic acid (DBSAH) and dinonylnaphthalenesulfonic acid (DNNSAH) are typical examples of such dopants; the solubilities of the complexes have been shown to increase with the increasing amount of dopant.[13−15] Thus, PANi doped with DBSAH represents a polymer−surfactant system Fredrickson used in the predictions, and the observed chain expansion in dilute solutions can be related to Fredrickson’s calculations.

Polymer−surfactant systems have also been shown to organize in solid state into liquid crystalline phases depending on the molecular nature of the components and preparation conditions.[16] Ikkala et al. have investigated supramolecular self-organized polymeric nanostructures using amphiphilic molecules (such as DBSA) with flexible polymers.[17] They have found that the structural features depend strongly on the nature of the amphiphilic molecules and on the applied external forces. Oscillatory shear flow studies also showed that the self-organized lamellae align parallel when sheared below order−disorder transition (ODT) and that the hydrogen bonds between the amphiphilic molecule and the polymer are strong enough to endure the applied external forces.[18,19] These studies with flexible polymers are unique as shearing studies with liquid crystalline polymers only show chain alignment under shearing when the liquid crystalline phase has been established and evidenced before the shearing.[20] In most of these studies, the liquid crystallinity is achieved by introducing a mesogenic unit in the polymer backbone and side chains. But as emphasized here, an amphiphilic surfactant and polymer complex can self-organize into liquid crystalline order without a mesogenic unit due to the simultaneous assembly of supramolecularity.[17,18,21]

Our previous research with undoped conducting polymers has also resulted in finding conformational changes during a phase transition of conducting polymers. Poly(alkylthiophene)s (PAT) in the undoped state

---

* To whom to address the correspondence.

10.1021/ma020146d CCC: $22.00

form layered structures, in which the layering is a function of the covalently attached alkyl side chains.[22] We have been able to show that the formation of the supramolecular structures results in conformational changes improving the planarity and at the same time increasing in the length of the conjugated segment. We observed in situ phase transitions (with thermal analysis and optical microscopy (OM) studies) while cooling PAT's and reported the occurrence of the conformational changes due to the ODT-type transition. This has previously been accounted for the decrease in thermal energy and to be independent of phase transitions. This finding is a strong support for the observation of chain extension in an ordered phase. We also applied manual shearing to PAT's similarly to the experimentation in this research and found out interestingly the formation of liquid crystalline structures. The observed Schlieren structures were shown to be dependent on the shearing and cooling conditions.[23,24] Thus, PAT's are not thermotropic liquid crystalline (LC) polymers as the thermal energy is not adequate to induce the LC phases, and PAT's resemble lyotropic polymers. Although there is no solvent in the polymer samples, the long alkyl side chains can be accounted for the "solution behavior" as they increase the mobility of the chains and allow the cooperational motion of the macromolecules to self-organize in these LC phases during the application of the external forces.

In the earlier work with PANi/DBSA complexes, we were able to observe limited birefringence but were not able to achieve viscoelastic behavior.[21,25] Our goal then was to increase the amount of surfactant molecules and then even to apply external forces for possible chain alignment to maximize the experimental conditions for the formation of liquid crystalline phases. In the present study, the amphiphilic molecules, both the dopant and the additional zinc salt, are not attached by covalent substitution but by interactive forces, but they still determine the supramolecular self-organization of the complex, as all the components arrange within each other depending on the interactive forces, both hydrophilic and hydrophobic.

The maximum amount for doping is restricted to a 1:0.5 mole ratio of PANi and dopant due to the amount of quinoid imine groups in PANi, but this amount has shown not to be adequate for optimal solubility. An excess amount of dopant, which forms hydrogen bonding with the amine groups in the PANi chains, is needed for the enhanced solubility.[26] These weakly interacting acid molecules are eventually able to migrate to the surface from the final product, thus causing a severe quality problem. It would be essential to find a way to improve the interaction of the excess dopant needed for solubility with PANi. Our plan in this work is to use a metal salt of a dopant; that is, the zinc salt of dinonylnaphthalenesulfonic acid as an additive of doped PANi as zinc is known to interact strongly with nitrogen atoms in macromolecules.

Experimental Section

Polyaniline (PANi), doped with dinonylnaphthalenesulfonic acid (DNNSAH), was supplied by Monsanto. The sample solution contains 34 wt % of the doped PANi, 9 wt % butylcellosolve, and 57 wt % xylene. Zinc $(DNNSA)_2$ is 50% solution in ethylene glycol monobutylethyl ether, supplied by King Industries. Chloroform, xylene, and toluene were all Aldrich products and were used as supplied.

PANi doped with DNNSAH is highly soluble in chloroform. The addition of the zinc salt was done in the chloroform solutions of the doped PANi in controlled weight ratios of doped PANi and zinc salt, namely, 1:0.5, 1:1, 1:1.5, and 1:2. All of the samples were stirred for 48 h at room temperature, and thin films were prepared on glass microslides by evaporating the solvent under ambient conditions.

An UV−vis spectrometer DMS-100 from Varian Co. was applied for the investigation of the degree of doping. All films were studied before and after heat and shear. Samples were scanned from 200 to 900 nm with a scanning rate 10 nm/s.

An UV−vis−near-infrared spectrometer (Shimadzu Scientific Instruments Inc.) was used to study the near-IR region. The instrument with a double-beam source connected to a photomultiplier R-928 for the ultraviolet−visible region and PbS cell for the near-infrared region. Spectral behavior of sheared samples was studied from 260 to 2600 nm with a scanning rate 100 nm/min and resolution of 0.1 nm.

A Nikon Optiphot HFX-II optical microscope with a FX-35 A camera was used to study the morphological changes of all doped PANi/Zn salt complexes. The microscope is connected to a Mettler FP-82 hot stage with a FP-80 processor that controls the temperature. Thin polymer films were heated to different temperatures at a heating rate of 10 deg/min. At the selected temperature, the manual shear was applied on the top of the cover glass by pressing the cover with the tip of a spatula. The pressing action was a short back and forth movement on the cover in similar manner we have applied before to undoped conducting polymers.[24]

A Philips APD 3720 X-ray generator was used for wide-angle X-ray diffraction experiments. The point-focused beam was monochromatized to Cu $K\alpha$ with a graphite crystal. The X-ray source, a XRG 3100 generator, utilized the Cu $K\alpha$ target. The 2θ step size for each individual data collection point was set into 0.004°.

Conductivities of doped PANi/Zn salt complexes were measured by the four-point probe method. Four equally distanced probes were brought in close contact with the sample. The head is lowered onto the sample until the four probes make good contact with the sample. A constant current source is used to pass a steady current through the two outermost probes, and the voltage drop across the inner two is measured. The thickness of the films varied between 3 and 4 μm.

Results and Discussion

The zinc salt of DNNSAH was added to the doped PANi in weight ratios of 1:0.5, 1:1, 1:1.5, 1:2, 1:3, and 1:4 (in ratio of the doped PANi/Zinc salt) in chloroform. The initial PANi/dopant ratio was kept constant as received in the commercial Monsanto product. Thin films on glass slides were obtained after the evaporation of the solvent, a glass cover was placed on these polymer films, and the manual shearing was applied at 160, 180, and 210 °C by pressing the glass cover firmly back and forth with a spatula. The doped PANi films without the addition of the zinc salt were not shearable at any temperatures. The doped PANi/Zn salt complex weight ratios 1:0.5 and 1:1 showed a very small response to shear, as the film was shearable only at the edges of the films. The samples with the complex ratios of 1:1.5 and 1:2 were clearly different; shearing could be applied throughout the whole film, and the glass cover moved back and forth easily during the shearing with the spatula. The samples with 1:3 and 1:4 composition ratios could not be sheared due to the changed viscosity and stickiness with the glass surfaces; the large amount of excess surfactant started to dominate the melt behavior. The samples with 1:1.5 and 1:2 ratios and the shearing temperature of 180 °C were selected for the further studies, as the shearing at 160 °C was still not optimal

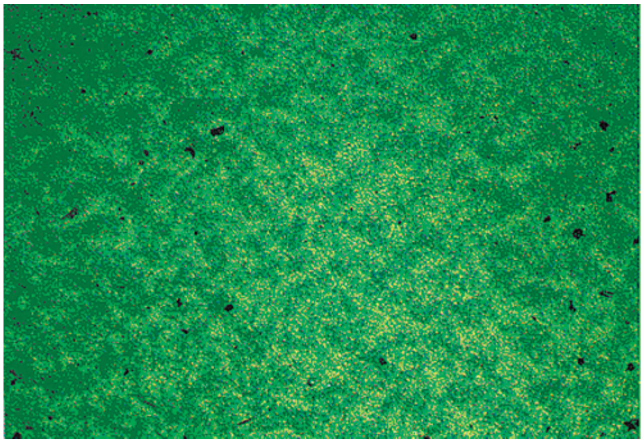

Figure 1. Optical microscopy picture of a doped PANi/Zn salt sample (1:1.5 ratio) before shear (magnification ×100).

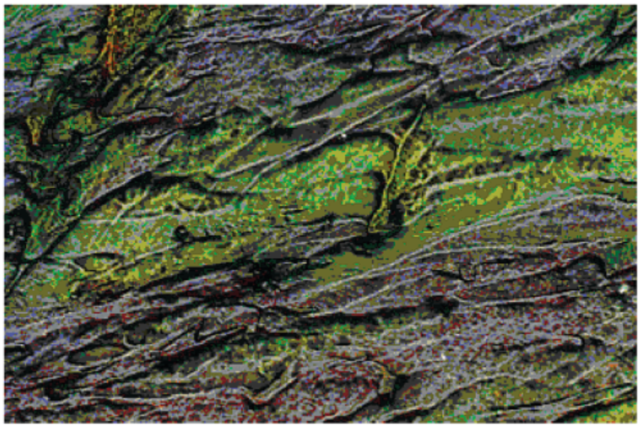

Figure 2. Optical microscopy picture of the doped PANi/Zn salt (ratio 1:1.5) at room temperature after shearing at 180 °C (magnification ×100).

Figure 3. Optical microscopy picture of the doped PANi/Zn salt (ratio 1:2) at room temperature after shearing at 180 °C (magnification ×100).

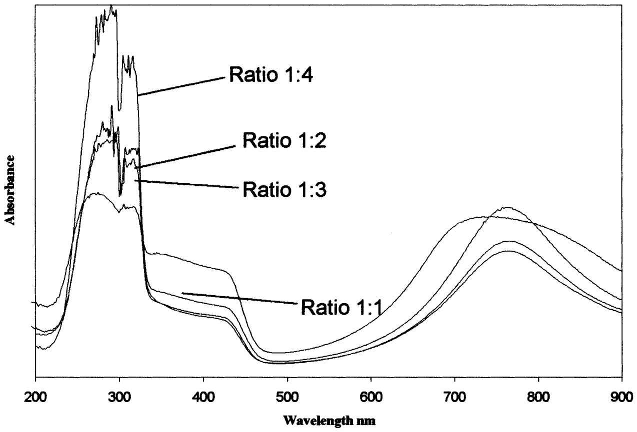

Figure 4. UV−vis spectra of the doped PANi/Zn salt samples before the shearing experiments at elevated temperatures.

due to the low temperature, and at 210 °C, thermal decomposition starts to be possible.

The samples were cooled to room temperature after the shearing at the elevated temperatures and were evaluated under an optical microscope (OM). An OM picture of doped PANi/Zn salt complex (ratio 1:1.5) before shear is shown in Figure 1. This picture has been taken under bright field and not under cross-polarized light (as no birefringence can be observed before the shearing). The color of all the films with different complex ratios was green, which is typical for doped PANi. After the shearing at 180 °C, the doped PANi/Zn salt complexes with ratios 1:1.5 and 1:2 showed different colors and structural features under cross polarized light at room temperature (RT) as shown in Figures 2 and 3. As can be observed in the pictures, a strong birefringence was developed when viewed under crossed polarized light. These birefringent images show the features of the directional shearing and resemble liquid crystalline behavior of the polymers.

The thin films of the doped PANi/Zn salt samples were also studied by UV−vis spectrometer. The UV spectra of the thin films of the doped PANi/Zn salt complexes with different weight ratios are shown in Figure 4. Two well-defined peaks can be observed in all samples: a peak at 420 nm and another peak at 755 nm. The absorption peak at 420 nm is due to the transition from the polaron band to the π^* while the transition from π band to polaron band causes the 755 nm absorption peak.[27,28] The fact that the adsorption peak at 755 nm is relatively sharp indicates that the polarons are localized. These spectra of doped PANi/Zn salt of DNNSAH are typical of that of doped PANi without a zinc salt. The addition of zinc salt does not seem to have any effect on the optical properties of doped PANi. (A doping effect of a zinc salt has been observed before,[29−31] but the phenomenon does not affect our approach as we started with samples that were first doped.)

The samples were sheared at 180 °C, cooled to room temperature, and investigated by a UV spectrometer. The UV spectrum of the doped PANi/Zn salt sample with the weight ratio of 1:1.5 (Figure 5) reveals changes after the shearing process at high temperature. The comparison of the sample with the ratio of 1:1.5 after heating and shearing (Figure 5) with the same sample before shearing (in Figure 4) shows that the maximum at 755 nm has disappeared and has been replaced by an extended absorption from 500 to 900 nm, which has been explained by the delocalization process of the polarons.[1−3] The localized polarons have been delocalized due to our experiment process. Identical results were obtained for sheared films of doped PANi/Zn salt with a ratio 1:2, and again, the localized polarons as evidenced before shearing for this sample changed to be delocalized.

The samples with complex ratios of 1:1.5 and 1:2 were further studied in the near-IR region to further confirm the extent of delocalization. Figure 6 shows the UV−NIR spectrum of the doped PANi/Zn salt samples in ratios 1:1.5 after the shearing at 180 °C. (The spectrum

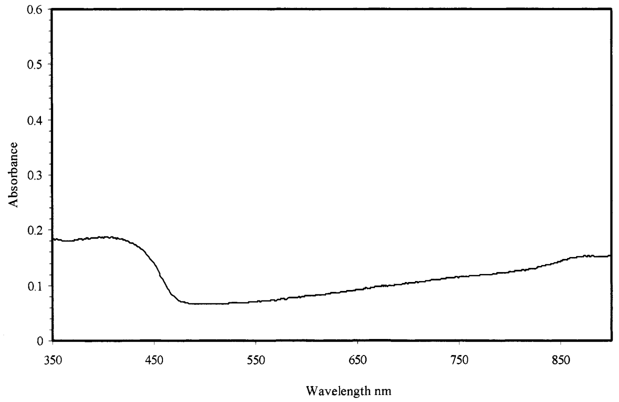

Figure 5. UV−vis spectrum of the sheared film of the doped PANi/Zn salt sample at a ratio of 1:1.5.

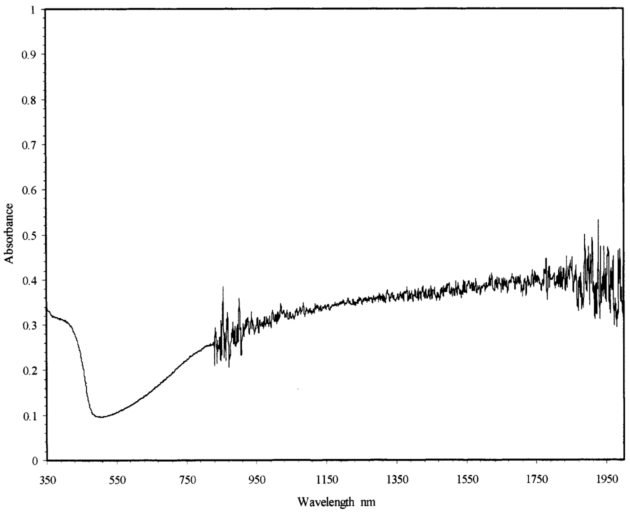

Figure 6. NIR spectrum of the sheared film of the doped PANi/Zn salt sample at a ratio of 1:1.5.

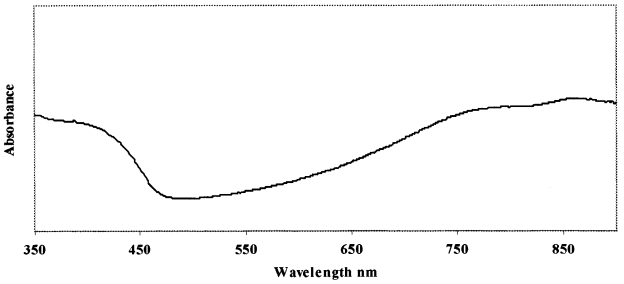

Figure 7. UV−vis spectrum of the doped PANi/Zn salt samples (1:1.5 ratio) at room temperature after heating to 180 °C without applying the shearing.

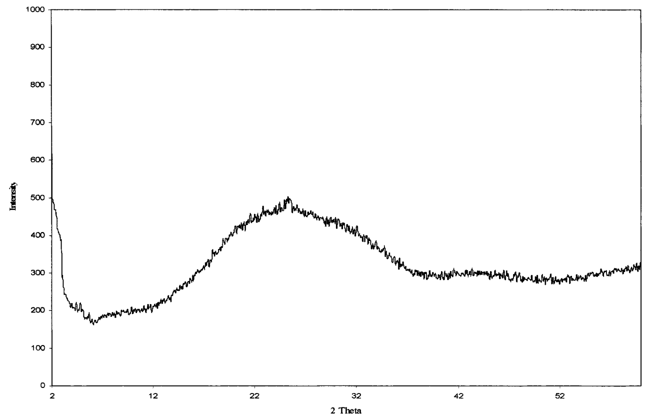

Figure 8. X-ray diffraction pattern of the doped PANi sample.

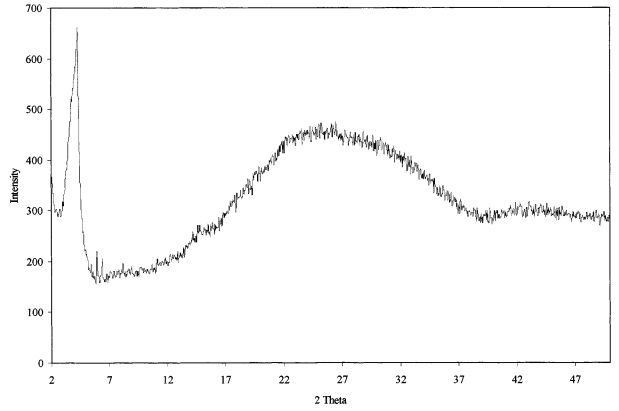

Figure 9. X-ray diffraction pattern of sheared film of doped PANi/Zn salt sample (1:1.5 ratio).

for the sample with complex ratio 1:2 has the same features.) A strong intensive free carrier tail extends from 1000 up to 2000 nm in both of the spectra, and this homogeneous free carrier tail is a further confirmation of the delocalization of the polarons induced by the shearing process.

To find out the influence of the elevated temperature without the shearing, a thin film of the doped PANi/Zn salt sample with a weight ratio of 1:1.5 was exposed to temperature of 180 °C for a time period comparable to the shearing experiment, cooled to the room temperature, and investigated by the UV spectrometer. The UV spectrum of the doped PANi/Zn salt sample in 1:1.5 ratio when heated only is shown in Figure 7. After heating the film, the localized maximum, which was observed at 750 nm before the heat treatment (Figure 4), was red-shifted to higher wavelengths and was clearly broadened. This observation may indicate that temperature only might have similar delocalization effect although the temperature effect alone on the UV spectrum is not as strong as the shearing effect at elevated temperatures. The main difference is that optical microscopy after the temperature effect only does not reveal any birefringent behavior as revealed after the shearing.

The above-shown optical microscopy studies revealed strong birefringence in these films after the shearing process. In the next step, we wanted to investigate whether new crystalline structures were developed in the sheared by using a wide-angle X-ray diffractometer. The X-ray diffraction pattern for the doped PANi without the added zinc salt (Figure 8) does not show any structural features, which is in accordance with the earlier research results.[15] This was somewhat surprising as it is well-known that PANi forms lamellar structures when doped with dodecylbenzenesulfonic acid (DBSA), and the distance between the layers for PANi/DBSA complex has been shown to depend on the dopant concentration and doping conditions.[21] The intensity of the reflections vs the angle pattern for the sample of 1:1.5 ratio, which was sheared at 180 °C, is shown in Figure 9. The complex of 1:1.5 ratio has a sharp peak at 2θ of 4.25° with a d spacing of 20.6 Å. Similarly, the complex with a ratio of 1:2 was found to have a sharp crystalline peak at 2θ of 4.25° with a d spacing of 20.8 Å. As evidenced with PANi/DBSA complexes, the low angle d spacing below 30−40 Å is dependent on the size and concentration of the dopant; thus, the layer distance of about 21 Å is a function of the dopant and additive size and concentration. Ikkala et al. found 31 Å as the layer distance for PANi/Zn(DBSA)$_2$ complex, but PANi was not doped before the addition of the zinc salt and was not sheared either.[29] The low value, 21 Å, found in our research is somewhat surprising but may be due to the shorter alkyl substituents (nonyl) in this study compared to the Pani/DBSA (dodecyl) results and because the shearing has additional packing effects.

The electrical conductivities of sheared doped PANi/Zn salt films were measured after the structural investigation. Thin films of doped PANi /Zn salt with a ratio 1:1.5 has a conductivity of 2×10^{-2} S/cm while doped PANi/Zn salt with a ratio 1:2 had a conductivity of 14×10^{-2} S/cm. As a reference, the electrical conductivity of a thin film of doped PANi was measured to be 13×10^{-6} S/cm. The observed enhancement of 3 orders of magnitude in the electrical conductivity of doped PANi complexes is consistent with the observed liquid crystalline phase.[17,18]

Our investigations show that four important phenomena have occurred during the shearing at elevated temperatures: (i) A liquid crystalline structure has been formed due to the shearing at elevated temperatures. (ii) The formation of this liquid crystalline phase induces chain extension in the PANi chains. (iii) This chain extension in this LC phase induces the delocalization of polarons as has been observed in liquid phase by MacDiarmid et al. (iv) The conductivity of the sheared increases due to the above molecular arrangement.

The formation of the liquid crystalline phase is clearly evidenced by the birefringent features observed under cross-polarized light using optical microscopy (OM) and confirmed by X-ray analysis, which shows the formation of layered structures. Our previous research on the structure formation in conducting polymers, but in the undoped state, results in similar understanding of the macromolecular behavior of these conducting materials. The chain expansion in this liquid crystalline phase is evidenced by the UV analysis, and it seems to be evident that we have been able to achieve similar delocalization of polarons in a liquid crystalline phase instead of the previously mentioned solution phase.[1−3]

The fact that the conductivity increases in our samples after the shearing at elevated temperatures is not a surprise: first of all, the achieved delocalization of polarons has been shown to result in increased conductivities,[1−3] and an optimal phase morphology has been shown to improve conductivities in ion-conducting systems.[17,18] We have also prepared liquid crystalline PANi samples in our parallel studies by using a mesogenic dopant. (The mesogen is attached covalently to the acidic dopant molecule.) In these studies,[32,33] we have been able to follow phase transitions kinetically with simultaneous optical and conductivity studies and have obtained confirming results on the conductivity dependence on the morphology.

References and Notes

(1) Xia, Y.; MacDiarmid, A. G.; Epstein, A. J. *Macromolecules* **1994**, *27*, 7212.
(2) Xia, Y.; Wiesinger, J. M.; MacDiarmid, A. G.; Epstein, A. J. *Chem. Mater.* **1995**, *7*, 443.
(3) Min, Y.; Xia, Y.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *69*, 159.
(4) Fredrickson, G. H. *Macromolecules* **1993**, *26*, 2825.
(5) Chiang, J. C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.
(6) Genies, E. M.; Lapkowski, M. *Synth. Met.* **1988**, *24*, 61.
(7) Chen, S. A.; Fang, W. G. *Macromolecules* **1991**, *24*, 61.
(8) Mantovani, G. L.; MacDiarmid, A. G.; Mattoso, L. H. C. *Synth. Met.* **1997**, *84*, 73.
(9) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 9. Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *55*, 3514.
(10) Mantovani, L.; Mattoso, L. H. C. *3rd Brazilian Polym. Conf.* **1995**, 30 Oct, 475.
(11) Ikkala, O. T.; Laakso, J.; Väkiparta, K.; Virtanen, E.; Rouhonen, H.; Järvinen, H.; Taka, T.; Passiniemi, P.; Österholm, J. E.; Cao, Y.; Andreatta, A.; Smith, P.; Heeger, A. J. *Synth. Met.* **1995**, *69*, 97.
(12) Vikki, T.; Pietilä, L. O.; Österholm, H.; Ahjopalo, L.; Kärnä, A. T.; Levon, K.; Passiniemi, P.; Ikkala, O. *Macromolecules* **1996**, *29*, 2945.
(13) Cao, Y.; Smith, P.; Heeger, A. J. US Patent No. 5 232 631, 1993.
(14) Levon, K.; Ho, K. H.; Zheng, W. Y.; Laakso, J.; Kärnä, T.; Taka, T.; Österholm, J. E. *Polymer* **1995**, *36*, 2733.
(15) Kinlen, P. J.; Liu, J.; Ding, Y.; Graham, C. R.; Remsen, E. E. *Macromolecules* **1998**, *31*, 1735.
(16) Antoinetti, M.; Condrad, J.; Thunemann, A. *Macromolecules* **1994**, *27*, 6007.
(17) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkela, T.; Serimaa, R.; Ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557.
(18) Mäkinen, R.; Ruokolainen, J.; Ikkala, O.; De Moel, K.; Ten Brinke, G.; De Odorico, W.; Stamm, M. *Macromolecules* **2000**, *33*, 3441.
(19) De Moel, K.; Mäki-Ontto, R.; Stamm, M.; Ikkala, O.; Ten Brinke, G. *Macromolecules* **2001**, *34*, 2892.
(20) Hamley, I. W.; Davidson, P.; Gleeson, A. J. *Polymer* **1999**, *40*, 3599.
(21) Zheng, W. Y.; Wang, R. H.; Levon, K.; Rong, Z. Y.; Taka, T.; Pan, W. *Macromol. Chem. Phys.* **1995**, *196*, 2443.
(22) Hsu, M.; Ho, K.-S.;. Kwei, T. K.; Levon, K.; Myerson, A. S. *Macromolecules* **1993**, *26*, 1318−1323, Ho, K.-S.; Laakso, J.; Levon, K.; Mao, J.; Taka, T.; Zheng, W.-Y. *Synth. Met.* **1993**, *55*−*57*, 384−387.
(23) Park, K. C.; Levon, K. *Macromolecules* **1997**, *30*, 3175.
(24) Park, K. C.; Levon, K. *Mol. Cryst. Liq. Cryst.* **1998**, *319*, 61, Levon, K.; Park, K. C.; Cai, C. *Synth. Met.* **1997**, *84*, 335.
(25) Kim, M. S.; Levon, K. *J. Colloid Sci.* **1997**, *190*, 17.
(26) Kärnä, T.; Laakso, J.; Savolainen, E.; Levon, K. European Patent EP 0 545 729 A1, 1993.
(27) Epstein, A. J.; McCall, R. P.; Ginder, J. M.; MacDiarmid, A. G. *Spectroscopy of Advanced Materials;* John Wiley & Sons: New York, 1991; pp 355−396.
(28) Stafström, S.; Brédas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464.
(29) Ruokolainen, J.; Eerikäinen, H.; Torkkeli, M.; Serimaa, R.; Jussila, M.; Ikkala, O. *Macromolecules* **2000**, *33*, 9276.
(30) Chen, S.-A.; Lin, L.-C. *Macromolecules* **1995**, *28*, 1239.
(31) Khalil, H. Ph.D. Thesis, Polytechnic University, New York, 2000.
(32) Pialkulkiat, S.; Levon, K., to be submitted to *Macromolecules*.
(33) Ahn, H. K.; Levon, K., to be submitted to *Macromolecules*.

MA020146D