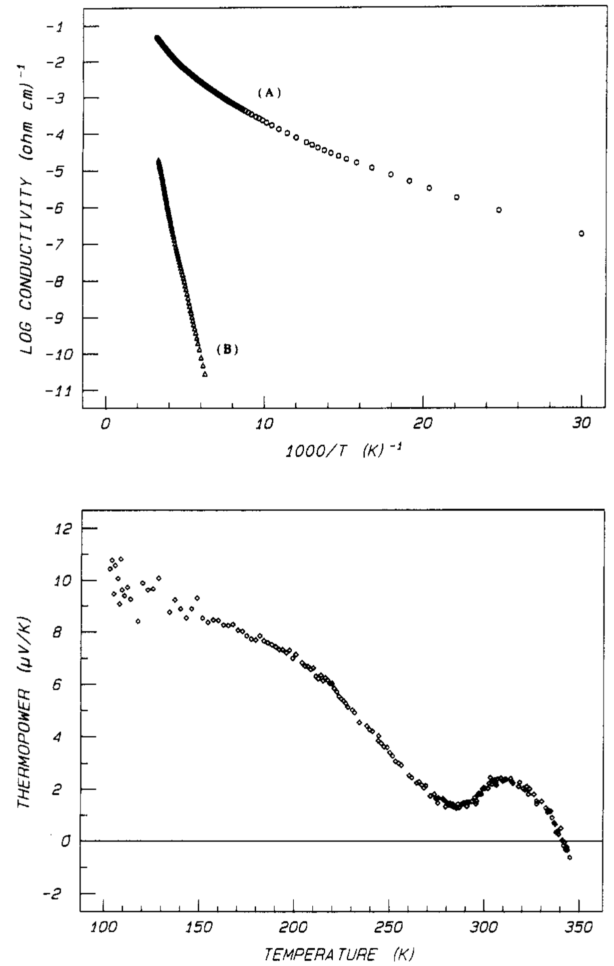

Figure 2. Top. curve (A): Four-probe variable-temperature electrical conductivity data of free-standing films of $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$ (I). Curve (B): pristine $V_2O_5{\cdot}1.6H_2O$ xerogel. Bottom. Variable-temperature thermoelectric power data for $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$.

Electron paramagnetic resonance, EPR, spectra (recorded at 273 and 77 K) of I show a broad signal observed at $g \sim 1.963$, which arises from interacting V^{4+} centers. The typical signal observed from polythiophene is absent suggesting the presence of antiferromagnetic exchange between the unpaired density on the polymer backbone and that in V_2O_5. The EPR signal of polythiophene[18] is observed only after the polymer is separated by dissolving the host matrix. These data show that in I phase separation to a polymer and a V_2O_5 phase does not occur. The EPR signal observed for I resembles that of $Na_{0.32}V_2O_5{\cdot}nH_2O$[19] and supports the proposed reduction of the V_2O_5 network in I.

As expected, free standing films of I show a dramatic increase in electrical conductivity by 4 orders of magnitude with respect to pristine xerogel with a room temperature value of $\sim 0.1\ \Omega^{-1}\ cm^{-1}$. Variable-temperature measurements (from 5 to 300 K) show a corresponding decrease in conductivity with falling temperature, characteristic of thermally activated behavior, similar to that observed for the bulk polythiophene polymer[20] (Figure 2). At room temperature the conductivity perpendicular to the films is at least 10 times lower than that parallel to them, indicating their anisotropic nature. Variable temperature thermoelectric power (TP) measurements show unusual behavior. At 350 K the Seebeck coefficient, S, is relatively small, $\sim -1\ \mu V/K$, and negative but quickly becomes positive (with a minimum at ~280 K) as the temperature falls and remains small and positive ($<10\ \mu V/K$) down to 100 K, the lowest temperature studied. The TP data suggest that at room temperature I is a p-type conductor with the predominant charge carriers being holes. The switch in conductivity above 340 K may suggest a change in the charge-transport mechanism with the majority carriers being electrons and the vanadium oxide layers assuming a more active role in the charge transport. The curious nonlinear temperature dependence of the TP, the carrier sign reversal, and the presence of the minimum at ~280 K currently are not understood. Thus far this phenomenon is unique to I and has not been observed previously in conductive polymer systems[21,22] or V_2O_5 xerogels.[19,22] It may be due to possible electronic interactions between the polythiophene polymer chains and the V_2O_5 layers or a hitherto unidentified phase transition.

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Registry No. $(C_8H_4S_2){\cdot}x^1/_2O_5$, 126457-61-2.

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Lewis Acid Complexation of Polymers: Gallium Chloride Complex of Nylon 6

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We report our concept of using Lewis acid complexation of polymers to modify polymer properties, mediate solubility and processing, and probe intermolecular interactions such as hydrogen bonding.

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Recently,[1-3] we reported that Lewis acid complexation of rigid-chain polymers such as poly(*p*-phenylenebenzobisthiazole) (PBT), poly(*p*-phenylenebenzobisoxazole) (PBO), and benzimidazolebenzophenanthroline-type ladder polymer (BBL) led to their solubility in organic solvents from which they could be more readily processed. Liquid-crystalline solutions of PBT were successfully prepared and processed by using such an approach.[3] The current interest in preparing molecular composites of rigid-rod and flexible-chain polymers from ternary solutions[4,5] suggested the need for exploring the same complexation-mediated solubilization approach in flexible-chain polymers. For example, molecular composites of PBT/nylon 66 have been prepared from ternary solutions in methanesulfonic acid.[4]

In this report we will use the flexible-chain polyamide nylon 6 to demonstrate all three aspects of our Lewis acid complexation approach mentioned in the first paragraph. In particular, we note that the semicrystalline nylon 6, which has been a commercial fiber-forming material for more than 50 years,[6] remains of theoretical and practical interest. Hence, any modification of its properties is also of general interest. Nylon 6, as with other polyamides, has a hydrogen-bonded structure in which N-H groups in a chain are hydrogen bonded to C=O groups in adjacent chains.[7] Thus, Lewis acid complexation would be a competing process to hydrogen bonding in the polymer since the possible complexation sites (NH and C=O) are also the hydrogen bond donor and acceptor sites. Hence Lewis acid complexation in combination with spectroscopic methods could be used to probe hydrogen-bonding interactions in the polymer.

The nylon 6 sample was obtained from Polysciences Inc. (Warrington, PA), and it has a glass transition temperature (T_g) of 57 °C, a melting point of 221 °C, and M_w = 24 000. The polymer sample was dried overnight in a vacuum oven at 60 °C to remove any moisture prior to use. Nitromethane (Aldrich, 99+%, bp 101 °C) and gallium(III) chloride (Aldrich, 99.99%, mp 78 °C) were used without further purification. The $GaCl_3$ complex of nylon 6 was prepared by adding a stoichiometric amount of polymer to a solution of $GaCl_3$ in nitromethane to give a 1:1 ($GaCl_3$:polymer repeating unit) complex. Depending on the polymer concentration, the mixture was stirred or heated to 40–50 °C until complete dissolution occurred. The solid complex was obtained from the solution by slow evaporation in a vacuum oven at 65 °C.

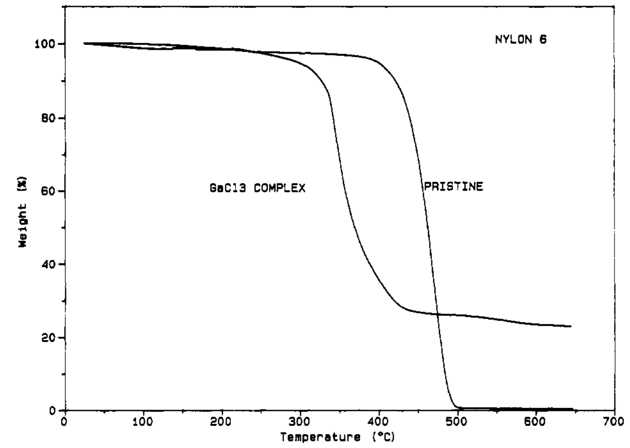

Figure 1. TGA weight loss curves showing the thermal stability of nylon 6 and $GaCl_3$–nylon 6 complex in nitrogen at 10 °C/min.

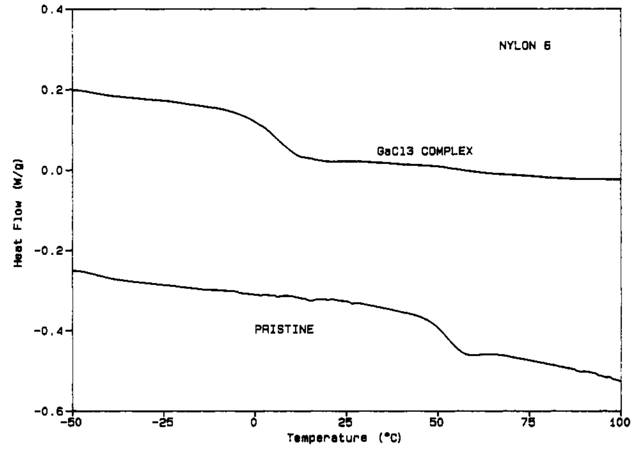

Figure 2. DSC thermograms of nylon 6 and its 1:1 $GaCl_3$ complex obtained at 20 °C/min.

Table I. Assignment of FTIR Spectra of Nylon 6 and Its 1:1 $GaCl_3$ Complex at 25 °C (cm^{-1})

sample	N-H stretch	amide I	amide II	CH_2 stretch[c]	CH_2 stretch[d]
nylon 6[a]	3293	1641	1558 (3095)[b]	2857	2930
$GaCl_3$–nylon 6	3363	1616	1549 (3095)[b]	2866	2946

[a] Regenerated from its $GaCl_3$ complex. [b] First overtone of amide II mode. [c] Symmetric CH_2 stretch. [d] Asymmetric CH_2 stretch.

Films of the $GaCl_3$–nylon 6 complex for infrared spectroscopy were prepared by solution casting onto NaCl substrates followed by slow evaporation of the solvent in vacuum at 65 °C overnight. Films of the pure nylon 6 were similarly prepared when the complex film was immersed in water to remove the Lewis acid and dried in vacuum at 65 °C for 12–15 h. Infrared spectra were collected on a Nicolet 20 SXC Fourier transform infrared (FTIR) spectrometer at room temperature (25–27 °C) under nitrogen purge. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were done using a Du Pont Model 2100 thermal analyzer using flowing nitrogen. Indium (mp 156.6 °C) DSC standard was used to calibrate the measured transition points; samples in sealed DSC pans were run at 20 °C/min. To facilitate observation of a clear T_g, the pristine nylon 6 sample was initially annealed by heating to 300 °C and rapidly cooling in air. TGA runs were performed at 10 °C/min.

The 1:1 $GaCl_3$:nylon 6 complex was found to be quite stable in solution and the solid state. Figure 1 shows the comparison of thermal stability of the complex and pristine nylon 6 in nitrogen as revealed by TGA. The nylon complex is found to be stable up to ~300 °C, whereas the pristine polymer starts to decompose at about 425 °C. It is noteworthy that the $GaCl_3$–nylon 6 complex has a unique single decomposition rather than two decompositions characteristic of the component materials.

The nylon 6 complex is soluble in organic solvents (e.g., nitromethane), forming viscous solutions, whereas the pure polymer is insoluble in nitromethane and many common organic solvents. This demonstrates that Lewis acid

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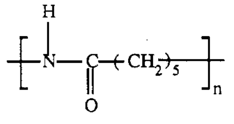
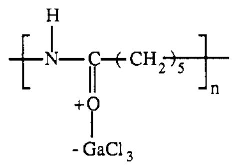
complexation can also mediate solubility of flexible chain polymers just as was found for rigid-chain polymers.[1-3]

Unlike pure nylon 6, which is highly crystalline and opaque, the $GaCl_3$–nylon 6 complex is an optically transparent, amorphous material. Figure 2 shows the DSC thermograms for both the pure nylon and its $GaCl_3$ complex. The T_g of the complex is found to be 7 °C (midpoint) compared to a T_g value of 57 °C (midpoint) of the pristine nylon 6; this is a 50 °C reduction in T_g due to Lewis acid complexation of the polyamide. These values of the T_g of the pristine nylon 6 and its $GaCl_3$ complex were reproducible for several samples in three repeated heatings up to 120 °C and cooling. This significant shift in T_g after complexation sugests an increase in polymer free volume and segmental mobility of the polymer chains. In this respect, the $GaCl_3$–nylon 6 polymer complex is more like a polymer with a bulky "side chain" than a plasticized polymer, although chain branching[8,9] and plasticization[9] can each lead to a T_g reduction. The very low T_g of the complex compared to the pure nylon 6 also suggests the absence of hydrogen bonds in the $GaCl_3$–nylon 6 complex. Further substantiation of the lack of hydrogen bonding in the complex was obtained from FTIR data described below.



$\left[\mathrm{N(H)}-\mathrm{C}(=\mathrm{O})-(\mathrm{CH_2})_5 \right]_n$

Nylon 6



$\left[\mathrm{N(H)}-\mathrm{C}(=\overset{+}{\mathrm{O}}-\overset{-}{\mathrm{Ga}}\mathrm{Cl_3})-(\mathrm{CH_2})_5 \right]_n$

$GaCl_3$ · Nylon 6

Table I shows the major bands and their assignment in the FTIR spectra of pure nylon 6 and its 1:1 $GaCl_3$ complex. The infrared bands of the pure nylon 6 in Table I are of the nylon 6 film regenerated from its $GaCl_3$ complex by precipitation in water. It is identical in all respects with the reported infrared spectrum for the pristine pure nylon 6.[10] This similarity of the infrared spectra of the nylon 6 recovered from its $GaCl_3$ complex and the pristine nylon 6 suggests the complete reversibility of the Lewis acid complexation. The complete recovery of the pure nylon 6 from its complex was further ascertained by the recovery of T_g, T_m, and insolubility in nitromethane. The pristine and regenerated nylon 6 samples were also insoluble, at 50–100 °C, in nitroalkanes, acetic acid, 3-chlorophenol, dimethyl sulfoxide, *N,N*-dimethylformamide, and chlorobenzene; hence intrinsic viscosity measurements could not be made to ascertain any possible change in molecular weight. These results show that the $GaCl_3$–nylon 6 solutions can be processed into the pure polymer films, coatings, or fibers. Furthermore, these results also suggest the feasibility of our envisioned processing of molecular composites of rigid-rod and flexible-chain polymers from ternary solutions of their complexes in organic solvents.[11]

A comparison of the FTIR spectra results for the pure nylon 6 and its $GaCl_3$ complex in Table I shows that the changes in the main bands are those anticipated for the severing of the N—H···O=C hydrogen bonds and complexation at the carbonyl oxygen site of the amide group. The N-H stretching band at 3293 cm^{-1} in the hydrogen-bonded nylon 6 is shifted to a higher frequency (by 70 cm^{-1}) in the complex. The amide I mode, which is known[12] to be dominated by the C=O absorption band, is shifted in the complex by 25 cm^{-1} to a lower frequency because of the greater electron-withdrawing effect of Lewis acid complexation at C=O than hydrogen bonding. Our FTIR results and their interpretation are confirmed by similar results and interpretation of the infrared spectra reported for BF_3 complexes of *N*-methylacetamide and related amide compounds.[13]

In conclusion, a stable 1:1 $GaCl_3$–nylon 6 complex has been prepared and found to be an optically transparent amorphous material in which the hydrogen bonds have been severed. The glass transition temperature of $GaCl_3$–nylon 6 was found to be reduced by 50 °C relative to the pure polymer. It was found that the pure nylon 6 was recoverable from its $GaCl_3$ complex by precipitation in water. These results demonstrate our concept of using Lewis acid complexation to modify polymer properties, mediate solubility and processing, and probe intermolecular interactions such as hydrogen bonding in polymers. Work in progress is investigating the Lewis acid–base chemistry of other aliphatic and aromatic polyamides, including solution- and solid-state properties of complexes and preparation of molecular composites.

Acknowledgment. We acknowledge support by grants from Amoco and General Electric Foundations.

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Preparation of Ultrathin, Size-Quantized Semiconductor Particulate Films at Oriented Mono- and Poly[(vinylbenzyl)phosphonate] Interfaces and Their Characterization on Solids

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We report here that vinylbenzyl phosphonate monomers and polymers, oriented at water–air interfaces, provide matrices for the size-controlled growth of semiconductor particles that can be transferred, essentially intact, onto solid substrates.

Preparations of $(C_{16}H_{35}O)_2P(=O)CH_2C_6H_4CH=CH_2$ (VBP), poly(styrenephosphonate diethyl ester) (PSP), and

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