Table III
Results of Characterization of Polyureas

	polymer		
	3	4	5
s	0.05	0.89	0.47
$[\eta]$,[a] dL/g	0.38	0.33	0.57
$\bar{M}_n$(^{1}H NMR)[b]	3200	1700	4300
$\bar{M}_n$(VPO)[c]	2800	2000	
$\bar{M}_w$(SE)[d]			5000
$\bar{M}_z$(SE)[d]			11600
T_t,[e] °C	363	356	353
ΔH_t,[e] kJ/mol	78	62	54
solubility[f] (nonsolvent/solvent ratio)	0.38	0.50	0.54
WAXS band: 2θ,[g] deg	20.5	19.8 (sh)	20.0
	21.6 (sh)	21.1	21.3
	25.7	26.0	25.5

[a] In Me_2SO/LiCl (2%) at 30 °C. [b] By end group analysis. [c] The polymers were N-trifluoroacetylated by trifluoroacetic anhydride in methylene chloride under nitrogen,[15,16] and $\bar{M}_n$ was determined by VPO in acetone at 25 °C. Degrees of trifluoroacetylation, determined by quantitative ^{19}F NMR (Bruker WH-90), were 0.46 (3) and 0.47 (4). The intrinsic viscosity of 4 dropped to 0.11 dL/g on trifluoroacetylation but increased again to 0.27 dL/g on hydrolysis of the trifluoroacetylamide groups. [d] By sedimentation equilibrium runs in DMF/LiCl (0.03%) at 30 °C (Beckman E), with spectrophotometric determination of concentration at λ = 284 nm. [e] By DSC (Mettler 30). The first endothermal transition was measured at different heating rates, and transition temperatures were obtained by extrapolation to zero heating rate. Results are averages of at least three runs. [f] See ref 14. [g] From wide-angle X-ray diffraction (Seiffert). "sh" stands for "shoulder".

the case of the polymer with essentially head-to-tail structure, **4**, which is by far the most regular one of this structural type described to date, the observed regularity is still substantially lower than the theoretical value. Transamidation in the polymer chain does not seem likely under the chosen reaction conditions, and we attribute the discrepancy between experiment and theory to the fact that the very high reaction rates cause the polycondensation to be partially mass transport controlled, even though the rate of mixing was rather high. Molecular mass average of the polymers **3**, **4**, and **5** were obtained by dilute solution viscometry, vapor phase osmometry, and ultracentrifugation. Structural characterization was performed by ^{1}H and ^{13}C NMR, IR, differential scanning calorimetry, and WAXS. Solubility was determined as reported previously.[13,14] Results are collected in Table III.

Melting points (i.e., the first endothermal transition) of the three polymers are surprisingly similar, contrary to the experience with polyamides,[4,7] where structurally regular and irregular polymers melt at temperatures rather far apart. The enthalpies of this process are larger for the structurally regular polymers than for the irregular one, as one would expect. Solubility is somewhat lower in **3** than in the other two samples, but **4** is almost as soluble as **5**. Part of this surprising phenomenon might be due to the fact that the irregular polymer, **5**, is of higher molecular mass than the two relatively regular ones.

Structural regularity is indeed controllable in polyureas, and relatively high degrees of regularity can be achieved for head-to-tail as well as for head-to-head/tail-to-tail polymers.

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(3) s is the probability of two adjacent –ab– units to point in the same direction: s = [accb]/([acca] + [accb] + [bccb]), where [accb] also includes –bcca– sequences.

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(11) In the extreme case where –bX reacts very much more slowly than –aX, and where –accY and –bccY react very much more slowly than YccY, the dimer XbaccY is formed almost exclusively in the early stages of the reaction. This then polymerizes to $(1/n)$X(bacc)$_n$Y, and s = 1.

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(14) Solubility of the three polymers was quantified by titrating solutions of 1–10 mg of polymer per mL of Me_2SO/LiCl (5%) with methanol at 30 °C. The volume ratio (nonsolvent/solvent) at the onset of turbidity was used; concentration dependence was found to be negligible.

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Received November 9, 1984

Poly(ethylene imine)–Sodium Iodide Complexes

Polymers offer the potential of being used as solid electrolytes because of their ability to be formed into thin films and the ability of some polymers to dissolve salts and transport ions. Poly(ethylene oxide) (PEO) has been shown to interact so strongly with some of the alkali metal salts that a high-melting crystalline complex is formed which involves approximately 4 mol of monomer units per mole of salt.[1] Although early work focused on this crystal complex, it is now generally believed that the transport of ions occurs primarily in the noncrystalline regions of the polymer.[2–4] The crystal complex is a manifestation of the strong interaction between ions and polymer and serves the useful purpose of providing mechanical rigidity at temperatures between 60 and 180 °C where the polymer would otherwise flow. A few other polymers containing high concentration of polar groups and high flexible chains have been reported to dissolve salts. These include poly(propylene oxide)[5–7] ($-[CH(CH_3)CH_2O]_n-$), poly(epichlorohydrin)[8] ($-[CH[CH_2Cl]CH_2O]_n-$), and, more recently, poly(ethylene succinate)[9,10] ($-[O(CH_2)_2-OC(O)-(CH_2)_2C(O)]_n-$). We now present evidence to indicate that linear poly(ethylene imine) ($-[CH_2CH_2NH)]_n-$) can dissolve salts and, in the case of NaI, form a high-melting crystalline complex.

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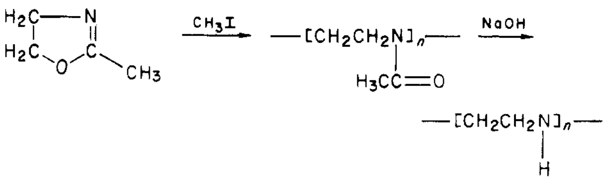
Linear poly(ethylene imine) was synthesized following the procedure of Saegusa et al.,[11,12] in which methyl iodide was used to initiate the ring-opening polymerization of 2-methyloxazoline in dimethylformamide to yield poly(*N*-acetylethylene imine). The polymer was then hydrolyzed in 2.5 N NaOH at 100 °C to yield linear poly(ethylene imine):



(1)

The polymer was washed with cold water until the filtrate was neutral and then dried under vacuum while it was slowly heated to 100 °C. Analysis for C, H, and N indicates the polymer is about 97% pure and the molecular weight as determined by GPC in chloroform solution was 2000.

Solid solutions of sodium iodide in the poly(ethylene imine) were prepared by dissolving both components in acetonitrile at 80 °C, cooling the solution to room temperature, and evaporating the solvent under vacuum. [PEI is insoluble in CH_3CN at 23 °C but is "salted-in" by the presence of dissolved NaI.] Final removal of solvent was accomplished under vacuum at temperatures just below the melting point of the sample (60 °C for NaI contents up to 0.1 mol/mol of monomer repeat and 100 °C for high concentration of NaI). Dried samples were stored in sealed containers within an argon-filled drybox. Samples containing the iodide salt were slightly more yellow than the starting material, which may indicate some oxidation of I^- to I_2.

Differential scanning calorimetry (DSC) was performed on samples hermetically sealed in the drybox using a Perkin-Elmer DSC II[13] equipped with a thermal analysis data station. Heating and cooling rates were usually 20 K min^{-1}.

Powder X-ray diffractometer scans were obtained by using Cu Kα radiation, a diffracted beam monochromator, a θ-compensating slit, and a Philips diffractometer.[13] Powdered samples were compressed into a cavity in a glass slide and covered with beryllium foil using Dow Corning[13] 340 silicone heat sink compound as a sealant within the inert atmosphere of the drybox.

Conductivity was deduced from Cole–Cole plots of impedance[14] obtained over a frequency range from 100 Hz to 13 MHz using thin stainless steel disks as electrodes. After samples were placed in the measurement cell but prior to the conductivity measurements, further steps were taken to remove residual solvent or moisture. First, samples were evacuated at room temperature for at least 1 day (7 days in some cases) and they were heated to the maximum temperature of measurement and evacuated for an additional 10–20 h. Samples were then cooled slowly to room temperature and the conductivity measurements were made upon increasing temperature again.

DSC traces of PEI and PEI with added NaI in molar ratios of NaI/(CH_2CH_2NH) from 0.05 to 1.0 are shown in Figure 1. The strong interaction of salt with the polymer is first evidenced by a decrease in crystallinity of the polymer, and at a molar ratio of 0.15, crystallization is completely prevented. At higher concentrations, a new endotherm appears in the vicinity of 150 °C. We interpret this to be a specific crystalline complex formed between the NaI and PEI analogous to that of PEO and several alkali metal salts.[1,2] [The melting point of NaI is 651 °C.] Once melted, the complex does not recrystallize upon cooling at the rate studied nor does it recrystallize after 1 month at room temperature.

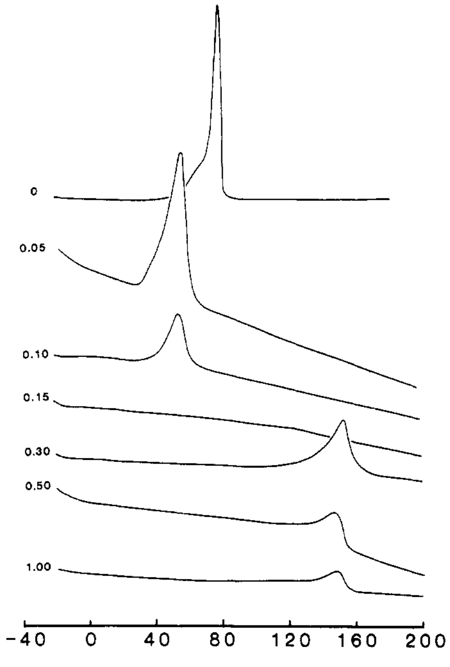


Figure 1. DSC traces of linear poly(ethylene imine) at 20 K min^{-1} containing the molar ratios of NaI to monomer indicated on the curves. The curve for polymer without added salt has been reduced in intensity by a factor of 3. Each curve responds to the same total weight of polymer and salt.

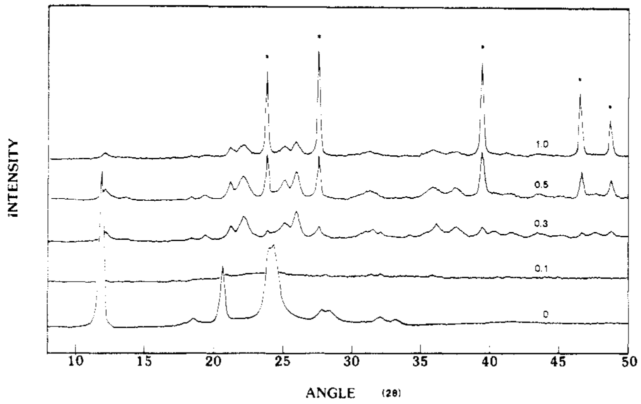


Figure 2. X-ray intensity vs. diffraction angle (2θ) for Cu Kα radiation from powdered samples of linear poly(ethylene imine) containing the molar ratios of NaI to monomer indicated on the curves. Asterisks indicate diffraction from anhydrous NaI crystals.

X-ray diffractometer scans of the polymer and polymer–salt mixtures are shown in Figure 2. The crystal structures of PEI and a series of hydrates have been reported by Chatani et al.[15-17] The diffraction maxima reported here are consistent with those reported for the anhydrate form[15]—especially the strong peak at a value of 2θ near 12°. For concentrations of NaI which prevented crystallization of PEI as seen in DSC, no crystal diffraction peaks are seen in the X-ray data. Note that the NaI must be dissolved in the polymer because no discrete peaks due to the NaI crystals are present at concentrations below a molar ratio of 0.3. For molar ratios of salt equal to or greater than 0.3, diffraction maxima are observed at positions different from those to be expected from either the pure PEI or the NaI, which indicates the formation of a crystalline complex. [We have been unable to obtain oriented polymer–salt samples for fiber patterns because of the low molecular weight.] Diffraction peaks from un-

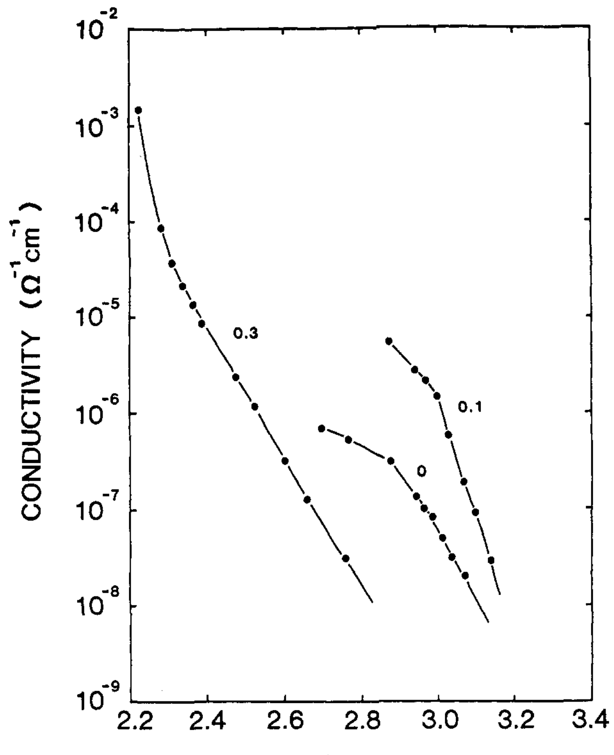


Figure 3. Conductivity as a function of reciprocal temperature for linear poly(ethylene imine) containing the molar ratios of NaI to monomer indicated on the curves. All data were obtained upon increasing the temperature.

dissolved, uncomplexed NaI crystals [indicated by asterisks in Figure 2] are first seen at a molar ratio of 0.3 and increase in intensity as the salt concentration is increased beyond that point. In other words, NaI in excess of 0.3 mol/mol of (CH_2CH_2NH) does not dissolve in or complex with the polymer but remains as a separate phase.

The dc conductivity as deduced from complex impedance measurements is shown as a function of reciprocal temperature in Figure 3. Data are for PEI containing 0.1 and 0.3 mol of NaI per mole of monomer repeat unit. We presume that the conductivity exhibited by the polymer to which we have not purposely added salt is due to ionic impurities, most likely sodium hydroxide left from the hydrolysis step in the synthesis of the polymer. The change in slope of conductivity vs. T^{-1} occurs when the semicrystalline polymer melts near 75 °C for the pure polymer and near 60 °C in the presence of 0.1 mol of NaI per mole of monomer. No evidence for a phase change below 150 °C is seen for the sample containing 0.3 mol of NaI per mole of polymer. Upon addition of 0.1 mol of NaI per mole of monomer repeat, the conductivity in the polymer at 60 °C increases from 6×10^{-8} $(\Omega\ cm)^{-1}$ to 1.5×10^{-6} $(\Omega\ cm)^{-1}$. However, when the molar ratio of NaI to polymer is increased to 0.3, conductivity is greatly reduced below values obtained before the purposeful addition of salt. Only at temperatures above 120 °C does the conductivity of the polymer containing 0.3 mol of NaI per mole of monomer exceed that of the starting polymer. The maximum in conductivity as a function of salt concentration has been observed in other polymer–salt systems[3,57] but the "pure" polymer has the lowest conductivity in those systems. As mentioned above, we have no assurance that all of the NaOH from the hydrolysis step has been removed from our sample. Steps were taken to remove the solvent used in preparing the films and precautions were taken to exclude moisture in subsequent steps as stated previously.

Linear poly(ethylene imine) has been shown to dissolve sodium iodide up to a maximum concentration of about 0.3 mol of NaI per mol of monomer repeat unit. At low concentrations, the salt interferes with the ability of the polymer to crystallize while at higher concentrations, the salt and polymer form a complex crystalline phase which melts near 150 °C. After melting the complex crystalline phase which formed upon evaporation of a mutual solvent for polymer and salt, it does not re-form upon cooling at the rates studied. The conductivity of the poly(ethylene imine) containing 0.1 mol ratio sodium iodide is 5×10^{-6} $(\Omega\ cm)^{-1}$ at 75 °C, which is lower than the values commonly obtained for salt-containing poly(ethylene oxide). The demonstrated capability of nitrogen-containing polymers to dissolve salts as well as oxygen-containing polymers may help in the understanding of solid polymeric electrolytes with enhanced ionic conductivity near room temperature.

Acknowledgment. Partial support by the Office of Naval Research is gratefully acknowledged.

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Received November 14, 1984

New Route to Carbon Fibers: Pyrolysis of Poly(cyanogen)

In a recent paper,[1] we have described the electropolymerization of cyanogen (ethanedinitrile) in acetonitrile containing an organic electrolyte. A poly(cyanogen) (PCN) having the structure $[C(CN){=}N]_n$ is obtained with a molecular weight of approximately 5000. Because the reaction involves formation of the heterocyclic anion

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