Structure of the Soluble Lewis Acid Poly(*p*-phenylenebenzobisthiazole) and Poly(*p*-phenylenebenzobisoxazole) Complexes

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The published postulated structures of the species present in aluminum chloride containing nitromethane solutions of PBZT and PBO have been reinvestigated. Consideration of previously reported and new ^{27}Al NMR spectra indicate that the predominant species in solution are $AlCl_4^-$ and a cationic species containing aluminum bound to the nitrogen atoms in the polymer repeat unit, which are formed by reaction of the neutral aluminum chloride complexed polymer. Calculational evidence is also presented to support a 2:1 ratio of aluminum chloride to polymer repeat unit in the neutral complex.

Introduction

Over the past five years several publications have appeared describing the solubilization of poly(*p*-phenylenebenzobisthiazole) (PBZT) and its oxazole analogue poly(*p*-phenylenebenzobisoxazole) (PBO, Figure 1) and other intractable polymers in nitromethane solvent containing Lewis acids.[1] Figure 2A shows the structures which have been proposed in ref 1 for the solubilized repeat units of PBZT and PBO (hereafter the symbol PBX is used to represent either PBZT or PBO) where the Lewis acid is aluminum chloride. Structures 2A are based primarily on the observed 4:1 Lewis acid:(PBX repeat unit) stoichiometry required for polymer solubilization in nitromethane.

On the basis of ab initio calculations on the benzthiazole complexes shown in Figure 3, supported by experimental data from the literature, which indicate that benzthiazole complexes hard Lewis acids only at the nitrogen atom, Connolly and Dudis suggested the Al_2Cl_6 complex (T3) shown in Figure 3 as a model structure for the actual (complexed) PBZT repeat unit in which the observed 4:1 Lewis acid:(polymer repeat unit) ratio could be achieved.[2] More recently another report has appeared describing semiempirical molecular orbital calculations (using PM3 parameters) of the 4:1 $AlCl_3$:(PBZT model compound) complex shown in Figure 2B. The energy minimized molecular structure of 2B and the enthalpy change for the formation of it from $AlCl_3$ and uncomplexed model compound were given.[3]

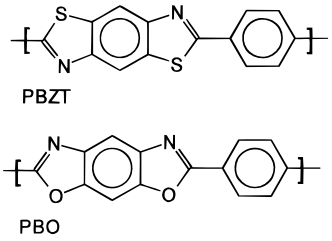

Figure 1. PBZT and PBO repeat units.

The Lewis acid mediated solubilization of rigid-rod polymers is an extremely important experimental finding, useful in structural and optoelectronic applications. It is important that the nature of the solute species in such solutions be better understood and consequently better use can be made of them. We present here information from the literature, new ^{27}Al NMR data, and computational results which require a reconsideration of the nature of the solute species in the $AlCl_3$/PBX/nitromethane solutions. We show that although experimentally 4 mol of aluminum chloride are required for each mole of polymer repeat unit for complete dissolution, it is not necessary nor even possible for

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

(1) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 1744 and references therein.

(2) Connolly, J. W.; Dudis, D. S. *Macromolecules* **1994**, *27*, 1423.

(3) Roberts, M. F.; Jenekhe, S. A.; Cameron, A.; McMillan, M.; Perlstein, J. *Chem. Mater.* **1994**, *6*, 658.

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there to be a 4:1 $AlCl_3$:(PBX repeat unit) complex in solution.

Experimental Section

Calculational Details. Calculational results reported here are from ab initio molecular orbital self-consistent-field restricted Hartree-Fock calculations done with the Gaussian92 suite of programs[4] using the 6-31G* basis set.[5,6] All structures were fully optimized. The (gas phase) D_e values in Figure 3 are calculated as the difference between the total energy of the structure shown and the sum of the total energies of the component structures. The reliability of these calculations, based on successful calculation of D_e of $AlCl_3 \cdot NH_3$, was discussed in ref 2.

NMR Experiments. PBZT and PBO fibers were provided by the Synthesis Group of the Polymer Branch, Air Force Materials Laboratories, Dayton, OH. Nitromethane (99+%), anhydrous aluminum chloride, and aluminum nitrate nonahydrate were obtained from Aldrich and used without further purification.

Dilute solutions of PBZT or PBO (typically 1 wt % polymer) in $AlCl_3/CH_3NO_2$ were prepared in a dry nitrogen atmosphere and were transferred into NMR tubes in a dry nitrogen-swept glovebag. The $AlCl_3$:(PBX repeat unit) ratio was 4:1 in these solutions.

^{27}Al NMR of the polymer−aluminum chloride complexes in nitromethane as well as aluminum chloride−nitromethane system were examined using a Varian XL 400 NMR spectrometer operating at 104.207 MHz. Delay time between pulse and FID acquisition was 30 μs. Delay between pulses was 1 s. Since the longest relaxation time (T_1) recorded for ^{27}Al is 160 ms,[7] this delay between pulses ensures the quantitative observation of the various ^{27}Al in solution. Data were collected over a spectral width of 150 to −50 ppm (21 000 Hz). The resonances were externally referenced (either in a coaxial NMR tube or separately prior to examining the samples) to the sharp signal due to the hexaaquo aluminum cation in a D_2O solution of $Al(NO_3)_3 \cdot 9H_2O$ (0 ppm).

Results and Discussion

There have been several ^{27}Al NMR studies of aluminum chloride dissolved in solvents of varying donicity and polarity. A common feature demonstrated in these studies is the tendency of aluminum chloride to disproportionate into $AlCl_4^-$ and a mixture of cationic species. This has been demonstrated in diethyl ether,[8] THF,[9] nitromethane,[10] and acetonitrile[11] solvents. Since $AlCl_4^-$ has a sharp ^{27}Al NMR signal, its identification is not difficult. Typically cationic species with coordination number four and six accompany the formation of $AlCl_4^-$. The cationic species, except for the symmetrical AlL_6^{3+} species, have broad signals with various chemical shifts (depending primarily on the coordination number and, to a lesser extent, on the cation charge and nature of the ligand). Consequently it has proved difficult to identify all cationic solute species.

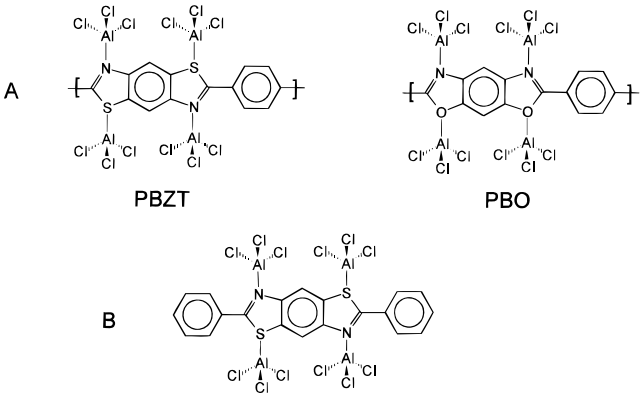

Figure 2. Proposed[1] structure (A) for solubilized PBZT and PBO and model structure (B) for solubilized PBZT.

In the cases where it has been investigated ($AlCl_3$/diethyl ether,[8] $AlCl_3$/THF,[9] and $AlCl_3$/nitromethane[10]), this disproportionation equilibrium has been shown to be temperature dependent, with the ionic species being favored at low temperature, and the tendency to ionize increasing with the coordinating power and dielectric constant[12] of the solvent. The natural ^{27}Al NMR line width of $AlCl_4^-$ is about 3 Hz,[13] but such a narrow line is seen only in systems where chemical exchange is slow on the NMR time scale, e.g., well below 0 °C in the systems described above.

^{27}Al NMR chemical shift data are often used to determine the coordination number of aluminum in solute species.[14] Normally for tetracoordinate aluminum, the ^{27}Al NMR signals are lower field than for hexacoordinate aluminum. Values from 148 to 34 ppm (using $Al(H_2O)_6^{3+}$ as an external reference) are quoted for tetracoordinate aluminum solutes. Hexacoordinate aluminum ^{27}Al NMR signals fall in a somewhat narrower upfield range between 40 and −46 ppm.[13] Relatively few data are available on chemical shift values for $AlCl_3 \cdot L$ species, where L is a neutral ligand. A range of 100 to 93 ppm has been reported for a small group oxygen donor ligands including ethers, carbonyl compounds, and nitroalkanes.[15]

The aluminum chloride/nitromethane (NM)/dimethylformamide (D) system has been investigated in detail,[16] and it makes an excellent model for the aluminum chloride/NM/PBX system which is of interest here. Equations 1, 2a, and 2b in Scheme 1 are an oversimplified set of equilibria showing some of the species in the $AlCl_3$/NM/D solution. Equations 3 and 4 (Scheme 1) by analogy apply to PBX in $AlCl_3$/nitromethane as described in the current work.

Equation 1 (Scheme 1) has been reported as the disproportionation equilibrium for the $AlCl_3$/NM system. This equation ignores the possibility of six-coordinate aluminum species, but, on the basis of new ^{27}Al NMR data presented below eq 1 appears to be correct. The equilibrium constant, based on conductivity data, for eq 1 is approximately 0.07 at room temperature. This value requires that all three species, i.e.,

(4) Gaussian 92, Revision C; Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1992.

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(10) a) Beattie, I. A.; Jones, P. J.; Howard, J. A. K.; Smart, L.; Gilmore, C. J.; Akitt, J. K. *J. Chem. Soc., Dalton Trans.* **1979**, 528. b) Dalibart, M.; Derouault, J.; Granger, P. *Inorg. Chem.* **1982**, *21*, 2241.

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(13) Akitt, J. W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987; Chapter 9, p 249.

(14) Akitt, J. W. *Prog. NMR Spectrosc.* **1988**, *21*, 1−149.

(15) Table 20 in ref 14.

(16) Schippert, E. *Adv. Mol. Relax. Proc.* **1976**, *9*, 167.

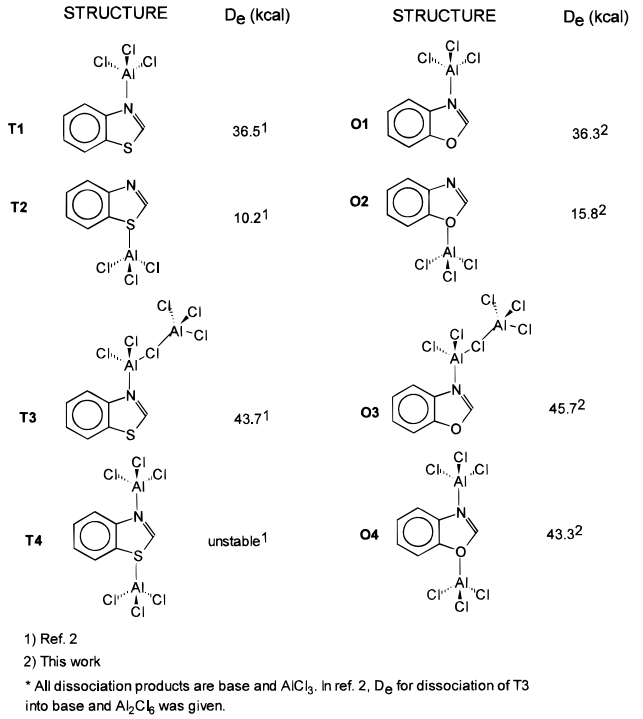

Figure 3. Calculated dissociation energies.

Scheme 1. Acid−Base Equilibria Involving $AlCl_3$

1) $2\ AlCl_3NM \rightleftharpoons AlCl_4^- + AlCl_2(NM)_2^+$

2a) $AlCl_3NM + D \rightleftharpoons AlCl_3D + NM$

2b) $2\ AlCl_3D \rightleftharpoons AlCl_4^- + AlCl_2D_2^+$

3*) $AlCl_3NM + PBX \rightleftharpoons AlCl_3(PBX) + NM$

4*) $AlCl_3(PBX) + AlCl_3NM \rightleftharpoons AlCl_4^- + AlCl_2(NM)(PBX)^+$

NM = Nitromethane

D = Dimethylformamide

PBX = PBZT or PBO

*These equations are written per mole of $AlCl_3$, each PBX unit has two binding sites.

$AlCl_4^-$, $AlCl_3$·NM, and $AlCl_2(NM)_2^+$, be present in measurable amounts simultaneously. As base D is added, NM is displaced from the aluminum chloride (eq 2a, Scheme 1) accompanied by the disproportionation equilibrium 2b. A sharp break in the change in proton chemical shift of NM vs solution composition at a D:$AlCl_3$ ratio of one indicates that the equilibrium constant for eq 2a is large. The equilibrium constant for disproportionation of $AlCl_3$·D (eq 2b, Scheme 1) increases as the temperature decreases, consistent with the observations on other systems mentioned above. Dimethylformamide is sufficiently small that the coordination number of aluminum can increase as the concentration of D increases, which allows several more solute species to occur at higher D concentration. (In the $AlCl_3$/NM/D system a large number of temperature-dependent equilibria occur concurrently, and the ^{27}Al NMR line widths of all solute species are consequently temperature dependent.) We have not included a description of the high D concentration equilibria in Scheme 1 since in the polymer solutions described here the base (polymer) concentration never gets high enough to warrant an expanded coordination sphere at aluminum, and our NMR spectra show no ^{27}Al signals in the 0 to −50 ppm region expected of six-coordinate cationic aluminum complexes.

Table 1. Relevant NMR Parameters[16]

species[a]	sym	^{27}Al chem shift (ppm)[b]	line width (Hz) (273 K)
$AlCl_4^-$	T_d	105.6	3
$AlCl_3D$	C_{3v}	97	29
$AlCl_2D_2^+$	C_{2v}	83	63

[a] D = dimethylformamide. [b] Relative to AlD_6^{3+} 0 ppm.

The possible formula of the polymer containing cationic species in the $AlCl_3$/NM/PBX system is derived from eq 4 in Scheme 1. We assume that the polymer repeat unit is too bulky to allow more than one to coordinate to a single aluminum atom. This formula is also consistent with the observed 4:1 $AlCl_3$:(polymer repeat unit) ratio,[1,17] which is the minimum value necessary for polymer solubilization to occur.

Table 1 lists ^{27}Al NMR line widths of some relevant species in NM. These values are for comparative purposes only, since these line widths are all temperature dependent. Nevertheless it can be seen that, as expected due to the quadrupole moment of the ^{27}Al nucleus, the ^{27}Al NMR line widths are quite dependent on the symmetry of the environment around the aluminum nucleus. The cationic PBX−aluminum species which we propose in Scheme 1 would have lower than C_{2v} symmetry about the aluminum. Its ^{27}Al NMR line width would be even broader than the small-molecule examples in Table 1 due to the long correlation time associated with the rotational motion of the polymer chains. Consequently we are unable to observe this species under our experimental conditions.

In Figure 4 are shown the ^{27}Al NMR spectra of a 2 wt % solution of $AlCl_3$/NM at −21 °C (a) and 1 wt % solutions of PBZT and PBO in 2 wt % $AlCl_3$/NM at −17 °C shown by (b) and (c), respectively. These spectra were scanned upfield to −50 ppm, but the lines shown are the only signals obtained. The molar ratio of the Lewis acid:(PBX repeat unit) is 4:1 in both polymer-containing solutions. Interpretation of these spectra is straightforward. On the basis of assignments from the literature[10b,12,16] and the information in Table 1, we assign the 104.5 ppm signal to $AlCl_4^-$ and the other signal at 98.8 ppm to $AlCl_3$·base. In Figure 4a the only base present is NM, so the 98.8 ppm signal is due to $AlCl_3$·NM. In Figure 4b,c, both polymer and NM are present. These solutions are rather complex as the variable-temperature analysis below demonstrates. It is not possible from the ^{27}Al NMR data here to determine the extent to which PBO and PBZT displace NM from the aluminum coordination sphere. However it is known that, in nitromethane, D quantitatively displaces NM from the aluminum coordination sphere (vide supra). Since both oxazoles and thiazoles are stronger bases than amides,[18] it would be expected that PBO and PBZT would also quantitatively displace NM.

The fact that there is still only one sharp ^{27}Al NMR signal at 98.8 ppm in solutions 4b and 4c requires explanation. To wit, either $AlCl_3$·NM, $AlCl_3$·PBZT, and $AlCl_3$·PBO all have the same ^{27}Al chemical shift to the limit of resolution of the instrument, or the signal at

(17) Venkatasubramanian, N.; Polk, M. B.; Kumar, S.; Gelbaum, L. T. *J. Polym. Sci., Polym. Phys. Ed.* **1993**, *31*, 1965.

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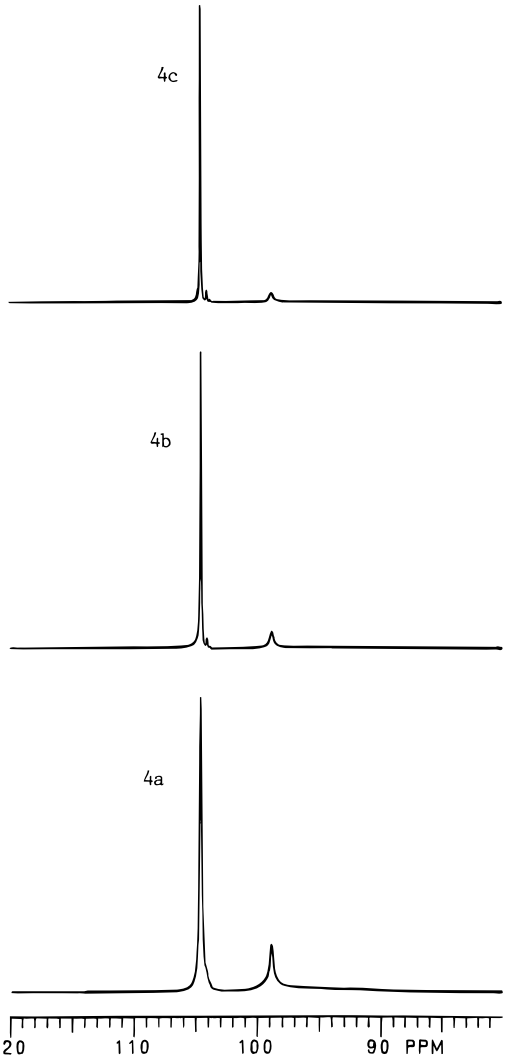


Figure 4. ^{27}Al NMR spectra of (a) 2 wt % $AlCl_3$/NM at 252 K, (b) 1 wt % PBZT in 2 wt % $AlCl_3$/NM at 256 K, and (c) 1 wt % PBO in 2 wt % $AlCl_3$/NM at 256 K.

98.8 is due to $AlCl_3$·NM in all three cases. If the 98.8 ppm signal is due only to $AlCl_3$·NM, that would imply that the $AlCl_3$·polymer signal is too broad to be observed under the experimental conditions, as described above. The fundamental conclusion of this paper is consistent with either interpretation, but assigning the same signal to the same species in all solutions involves the fewest assumptions, so we will proceed with the assumption that the 98.8 ppm signal is due to $AlCl_3$·NM in all cases.

There is a broad upfield signal in Figure 4a in the 90−92 ppm range, more evident when the spectrum is enlarged, which may be due to the cationic species, $AlCl_2(NM)_2^+$, which must be present in the same concentration as $AlCl_4^-$ according to eq 1. This signal is absent in Figure 4b,c. In these solutions the concentration of $AlCl_2(NM)_2^+$ would be lower, due to equilibria 3 and 4 (Scheme 1), and the polymer-containing cationic species which would replace $AlCl_2(NM)_2^+$ is expected to have an even broader line width.

Variable-temperature ^{27}Al NMR spectra are shown in Figure 5. Spectra 5a−c are from the $AlCl_3$/NM solution at 252, 297, and 334, respectively, while spectra 5d−f are from the PBO/$AlCl_3$/NM solution at 256, 324, and 354 K, respectively. Spectra similar to 5d−f were obtained for PBZT/$AlCl_3$/NM solutions as well. All spectra were scanned upfield to −50 ppm. The relevant chemical equilibria are shown in eqs 1, 3, and 4 in Scheme 1. In Table 2 are listed ratios of 98.8 ppm/104.5 ppm signals for the spectra shown in Figures 4 and 5. These ratios support the arguments which follow.

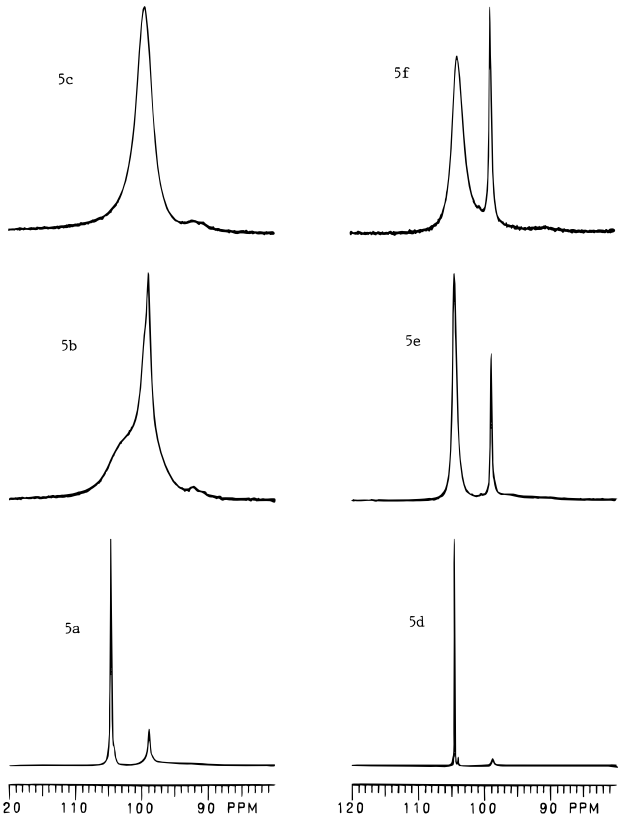


Figure 5. ^{27}Al NMR spectra of (a) 2 wt% $AlCl_3$/NM at 252 K, (b) 2 wt % $AlCl_3$/NM at 297 K, (c) 2 wt % $AlCl_3$/NM at 334 K, (d) 1 wt % PBO in 2 wt % $AlCl_3$/NM at 256 K, (e) 1 wt % PBO in 2 wt % $AlCl_3$/NM at 324 K, and (f) 1 wt % PBO in 2 wt % $AlCl_3$/NM at 354 K.

Table 2. Integration Data for Figures 4 and 5

figure	ratio of 98.8 ppm/ 104.5 ppm signals	figure	ratio of 98.8 ppm/ 104.5 ppm signals
4a	0.65	5c	
4b	0.26	5d	0.24
4c	0.24	5e	0.50
5a	0.65	5f	0.64
5b			

It is apparent from Figures 5a−c that the $AlCl_3$·NM disproportionation (eq 1, Scheme 1) has a similar temperature dependency to other $AlCl_3$·donor systems which have been studied (vide supra). Figure 5a is the same as Figure 4a. The signals are assigned to $AlCl_4^-$ (104.5 ppm) and $AlCl_3$·NM (98.8 ppm) as discussed above. Figure 5b is most readily interpreted as due to $AlCl_4^-$ rapidly exchanging with $AlCl_3$·NM. Qualitatively it also appears that the equilibrium has shifted toward the neutral species, $AlCl_3$·NM, as would be expected due to the increased temperature.[9,16] From Figure 5c it appears that this exchange is now rapid enough that only one signal can be seen. The change in chemical shifts from 5b to 5c is also consistent with a shift in the equilibrium toward the neutral species as temperature increases.

Given the chemical composition of the PBO/$AlCl_3$/NM system, it would be expected that the ^{27}Al NMR spectrum would contain several ^{27}Al NMR signals. Since spectra 5d−f contain only two signals, the interpretation of these spectra must be somewhat speculative. As mentioned above, the fewest assumptions involve as-

signing the 104.5 ppm signal to $AlCl_4^-$ and the 98.8 ppm signal to $AlCl_3$·NM. The remarkable conclusion to be drawn from these assignments is that the effect of the polymer in these solutions is to *retard the rate of the $AlCl_3$·NM disproportionation*. That is, spectrum 5e was obtained at 324 K and contains much sharper signals than spectrum 5b, which was obtained at 297 K. Also spectrum 5f still has two well-defined signals at 354 K, whose ratio is given in Table 2, while 5c shows only one signal at 334 K.

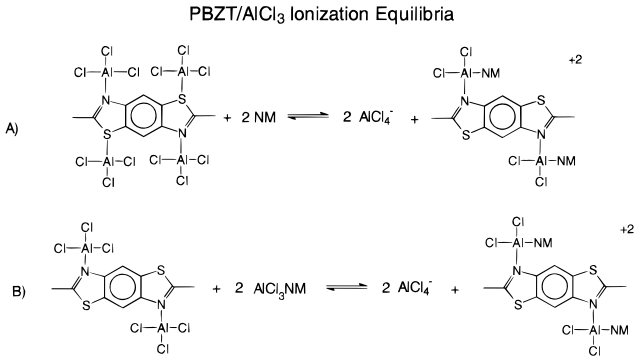
An explanation of this retardation of the rate of the $AlCl_3$·NM disproportionation can be obtained by considering eq 3 (Scheme 1), which describes the displacement of NM from the aluminum coordination sphere by polymer. As this displacement proceeds, the concentration of $AlCl_3$·NM decreases, and there is less $AlCl_3$·NM to exchange with $AlCl_4^-$ (eq 1, Scheme 1), which would slow down the ^{27}Al exchange as observed. In support of this, in spectra 4a−c, there does appear to be less $AlCl_3$·NM relative to $AlCl_4^-$ in the polymer containing solutions (4b,c) than the solution without polymer (4a) at a temperature low enough that exchange is slow on the NMR time scale. For this interpretation to be correct the equilibrium between $AlCl_3$·NM and PBX shown in eq 3 must be slow. A fast equilibrium 3 would make $AlCl_3$·NM available for reaction 1, and fast NMR exchange would then be expected. [A referee has correctly noted that the fact that, in spectra 5e,f, the $AlCl_4^-$ signal is broader than the $AlCl_3$·NM signal requires that there be at least one other exchange process involving $AlCl_4^-$ beyond those listed in Scheme 1. This observation points to the need for further experimental work to completely characterize this interesting system, but it does not invalidate the main conclusion of this work. We are grateful to the referee for this insight.]

Since the heterocycle N site in the PBX repeat unit is more basic than NM (vide supra), it is likely that $AlCl_3$·PBX, once formed, will heterolyze. Equilibrium 4 (Scheme 1) shows a one-step process which gives the expected overall 4:1 ratio of aluminum-to-polymer repeat unit. Alternatively, $AlCl_3$·PBX could disproportionate to form $AlCl_4^-$ and $AlCl_2$·$(PBX)_2^+$, and the $AlCl_2$·$(PBX)_2^+$ could then react with NM to form $AlCl_2$·(PBX)$(NM)^+$. In either case (1) formation of $AlCl_3$·PBX occurs at the expense of $AlCl_3$·NM and (2) further reaction of $AlCl_3$·PBX leads to formation of $AlCl_4^-$. This sequence of events produces a *larger* $AlCl_4^-$ concentration and a *smaller* $AlCl_3$·NM concentration, consistent with Spectra 5d−f. Given the evidence available at present, we can only assume that the polymer in these solutions exists as a mixture of $AlCl_3$·PBX and some cationic species in which the polymer is coordinated to aluminum.

The alternative interpretation mentioned above whereby the 98.8 ppm signal is due to both $AlCl_3$·NM and $AlCl_3$·PBX would not qualitatively alter the conclusion here. That is, if the $AlCl_3$·PBX species is observable at 98.8 ppm, from the sharpness of the 98.8 ppm signal, it must be exchanging with $AlCl_4^-$ much more slowly than $AlCl_3$·NM does in the absence of polymer.

Experimental evidence shown here shows that in the $AlCl_3$/NM/PBX system for both PBO and PBZT the predominant species present in the ^{27}Al NMR spectrum from 256 to 345 K is $AlCl_4^-$. The solutions were made using a 4:1 $AlCl_3$:(polymer repeat unit) ratio. Using the simplifying assumption, for the sake of clarity, that half

Scheme 2. PBZT/$AlCl_3$ Ionization Equilibria



of the aluminum in the solution is present as $AlCl_4^-$, it is evident that each polymer repeat unit has available to it only half of the aluminum in the solution. Thus, even though it requires at least 4 mol of aluminum chloride for each mole of polymer repeat unit to achieve solubilization of the polymer, each mole of polymer repeat unit has only about 2 mol of aluminum available to it for complexation.

The simplest interpretation of the ^{27}Al NMR data reported here is that the ^{27}Al NMR spectrum of $AlCl_3$·PBX has not been observed due to the breadth of its signal. A simple charge balance argument requires that if $AlCl_4^-$ is a major solute species, a comparable amount of cationic species must be present. Since the cationic species contains the polymer, the end result is that the neutral species is a minor solute species. Even so, still at issue is the nature of the neutral complex. Scheme 2 shows how either the structure in the literature[1] (A) or the structure we favor (B) could produce the same ionic species in the case of PBZT. A similar scheme would apply for PBO. We postulate structure B rather than structure A: based on the known coordination chemistry of benzthiazole,[2] the well-established hard and soft acid−base principle[19] and the numerical data which follow.

In Figure 3 we show a comparison of calculated dissociation energies of benzthiazole and benzoxazole complexes of aluminum chloride. The results are consistent with known chemistry, i.e., complexation with nitrogen is energetically preferred over either sulfur or, to a lesser extent, oxygen because the nitrogen atom is the more basic site in the molecule. The data in Figure 3 show that benzthiazole does not complex two separate aluminum chloride molecules. That is, when a single aluminum chloride complexes at nitrogen, the resulting structure will not complex an additional aluminum chloride at sulfur. This result and the reported limiting 4:1 $AlCl_3$:(PBX repeat unit) ratio led Connolly and Dudis to consider the Al_2Cl_6 complex, T3.[2] (Of course, in light of the present information it is not necessary to postulate a 4:1 complex at all.) We find that the main difference computationally between benzoxazole and benzthiazole as Lewis bases is that benzoxazole can bind two separate aluminum chloride molecules. That is, the bis-$AlCl_3$ complex, O_4, is calculated to be stable, as well as the Al_2Cl_6 complex, O3. The difference in dissociation energies between O3 and O4 is so small that we would predict that both types of complex species (bis-$AlCl_3$ and N·Al_2Cl_6) would be present in solution at the same time if the 4:1 neutral complex were to exist.

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Using the data in Figure 3, energy for gas-phase disproportionation of benzoxazole−N·$AlCl_3$, O1, into benzoxazole and benzoxazole−(N·$AlCl_3$)(O·$AlCl_3$), O4, can be calculated as $2(D_{e(O1)}) - D_{e(O4)} = 29.3$ kcal (26.9 if O3 rather than O4 is used), i.e., this reaction is quite endothermic. Similarly, disproportionation of T1 to benzthiazole and T3 also gives 29.3 kcal. Since all the species in question here are neutral and the number of polar dative bonds does not change from reactants to products, solvation effects should not greatly alter these results. Thus we conclude from the data in Figure 3 that the species T3 is unstable with respect to reaction with benzthiazole to form 2 mol of T1 and similarly O3 and O4 are both unstable with respect to reaction with benzoxazole to form 2 mol of O1. (The same type of argument would apply to the reaction of model structure 2B (Scheme 2) with its uncomplexed form, but this structure is too large for reliable ab initio calculations at present.) Since T3, O3, and O4 model the 4:1 $AlCl_3$·(PBX repeat unit) complexes, we further conclude that these should react with uncomplexed polymer to form the 2:1 complexes.

Since both aluminum chloride and the proton are hard acids, evidence about the protonated form of PBX polymers is relevant to the present study. Semiempirical (AM1) calculations on protonated PBX models[20] and ab initio calculations on oxazole,[20] thiazole,[20] and PBO models[21] show that the nitrogen atom is preferentially protonated. In methanesulfonic acid (MSA) solutions of PBO conductimetry results show approximately two protonations per repeat unit, which has been interpreted to mean that it is the nitrogen atom only which is protonated,[22] in agreement with the computational results. Although NM and MSA solvents are not the same, since absorption and emission spectra of PBZT/Lewis acid/NM solutions are quite similar to those of PBZT/MSA solutions,[1] we presume that results obtained in MSA solution are also applicable to aluminum chloride/NM solution. Therefore, by analogy, the above conductimetry results imply that only the nitrogen atoms in PBO are complexed by aluminum chloride in nitromethane. Since the sulfur atom in PBZT is a softer base than the oxygen atom in PBO, these results also imply that only the nitrogen atoms in PBZT are complexed by aluminum chloride. Complexation by an aluminum-containing cation, as depicted in Figure 6, would presumably produce a species which has a polymer electronic structure and spectrum similar to that of the protonated species.

As was mentioned in the earlier publication by Connolly and Dudis,[2] care should be taken in applying the results described here to other systems. No attempt has been made as yet to model computationally the gallium chloride complexes of PBX. The NMR spectra which have been reported on PBZT/gallium chloride/NM solutions[1] are broad and featureless and do not support any particular structure. Vibrational spectra of PBX·Lewis acid complexes, obtained on polymer films rather than solutions, have been interpreted in terms of 4:1 molecular complexes.[1] There is precedent for the mobile $AlCl_4^-$−$AlCl_2L_2^+$ equilibrium in solution to yield molecular species on solvent removal in vacuo.[23] The

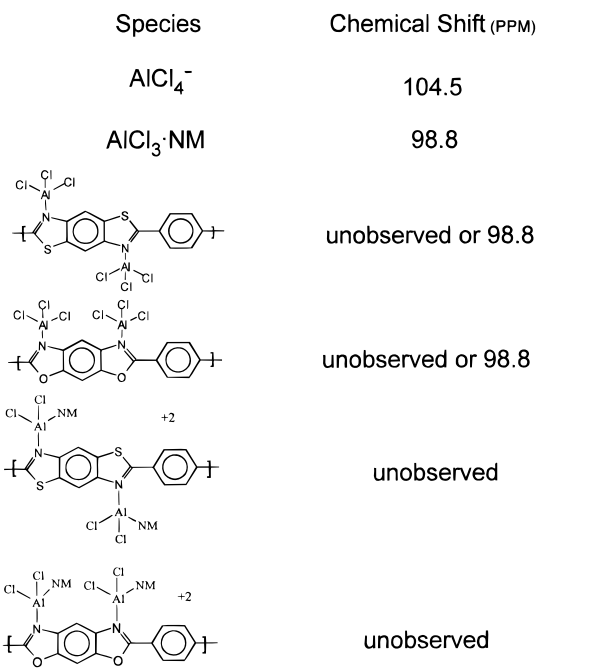

Figure 6. Aluminum-containing solutes in $AlCl_3$/polymer/NM solution.

arguments developed in this paper apply directly only to species present in solution, and we do not feel that they contribute to an understanding of the nature of the PBX·Lewis acid complex films which can be obtained on precipitation from solution.

Conclusion

^{27}Al NMR spectroscopy shows that the predominant observable aluminum species in $AlCl_3$/NM/PBX solution is $AlCl_4^-$. Unless each aluminum has more than one polymer molecule in its coordination sphere, it is therefore impossible for a 4:1 $AlCl_3$:(polymer repeat unit) species to be the predominant polymer-containing solute, based on stoichiometry. In addition, charge balance arguments require that the predominant polymer-containing solute be cationic. The simplest interpretation of the information at hand is to postulate the cationic species, $AlCl_2(PBX)(NM)^+$, shown in Scheme 2, as the predominant polymer-containing solute.

While it appears to be a relatively unimportant solute species, the nature of the $AlCl_3$·PBX is addressed computationally in this paper. Considering the energetics of a reaction between a 4:1 $AlCl_3$:(polymer repeat unit) complex and PBX, it is seen that the 2:1 $AlCl_3$:(polymer repeat unit) is the favored species. This is consistent with information from the literature on reactions of the proton with PBX, as well as with HSAB theory.

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