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Studies of the Stability of Poly(ethylene oxide) and PEO-Based Solid Electrolytes Using Thermogravimetry–Mass Spectrometry

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ABSTRACT: The thermal and oxidative stabilities of high molecular weight PEO and of solid electrolytes formed by dissolving divalent cation salts in PEO were studied in air and nitrogen using thermogravimetry–mass spectrometry. Certain cations had large effects on the stability of PEO, while the effect of different halide anions was less pronounced. Some electrolytes were found to degrade during the electrolyte formation process. At slower heating rates, the stabilities of PEO and $PbBr_2PEO_8$ were seen to be strongly influenced by traces of oxygen. The relationships between cation mobility and stability are discussed.

Introduction

Poly(ethylene oxide) (PEO) solutions of metal salts are unusual solid ionic conductors with potential applications that include electrolytes for battery and electrochromic devices. PEO-based solid electrolytes have been studied for a number of years,[1,2] but many, arguably most, aspects of their microstructure and local ion/polymer interactions are not well understood. This is especially true of systems incorporating inorganic multivalent metal salts, which have received much less attention than, for example, solutions of lithium salts.

Much of the current research on these materials is directed at characterizing and understanding the interactions between dissolved cations and the ether oxygens of the polymer chains. These help to define the overall conductivity of each composition and the mobility of each ion. This paper describes a study of the relationship between ion/polymer interaction and the stabilities of various PEO electrolytes containing multivalent cation salts.

A number of studies of the stability of pure liquid and solid PEO have already been reported. Madorsky and Straus[3] observed PEO to decompose above 300 °C into a variety of substances, including formaldehyde, ethanol, carbon dioxide, water, and many organic compounds in the range C_1–C_7. Bortel and Lamot[4] found similar species generated by the degradation of high molecular weight PEO and proposed mechanisms for their formation. Grassie and Perdomo Mendoza[5,6] studied the degradation of two samples of poly(ethylene glycol) (PEG; MW 1000 and 1500), which is low molecular weight PEO, both alone and complexed with ammonium polyphosphate and proposed mechanisms for the different degradation pathways observed in each case. They analyzed the degradation products and obtained results for pure PEO comparable to those of Madorsky and Bortel but found that water and 1,4-dioxane [$(CH_2CH_2O)_2$, a stable, cyclic ethylene oxide dimer] were the major degradation products of PEG complexed with ammonium polyphosphate. 1,4-Dioxane was not found to be a degradation product of pure PEG. Taoda et al.[7] studied the thermal cycling of 11 different molecular weights of pure PEO and showed that cycling at moderate temperatures (e.g., 30–150 °C daily in air) would almost completely volatilize even high molecular weight PEO in a few weeks. Although their work was performed in air, these authors isolated degradation products similar to those reported by Madorsky, Bortel, and Grassie, who worked under vacuum or inert atmosphere. Costa et al.[8] studied the thermal and oxidative degradation of PEO electrolytes containing NaSCN and $LiClO_4$ and found that these salts influence the stability and degradation mechanisms of PEO. Donbrow[9] summarized much of the published work involving the effect of oxygen on PEO and PEG at elevated temperatures and concluded that the ethylene oxide chain is not stable in the presence of oxygen. These studies show that the degradation of ethylene oxide is a complex process that is influenced by temperature, oxygen pressure, molecular weight, impurities such as catalyst residues or ionic species, and even crystallinity.

Previous studies have shown that the degradation of poly(ethylene oxide) is strongly affected by the presence of acidic salts.[5,6] However, relatively few reports describing the effect of ionic salts on the stability of PEO in solid forms have appeared,[8,10,11] which is somewhat surprising considering the interest in these materials as electrolytes. In the present study, the thermal and oxidative stabilities of pure PEO are compared with those of electrolytes made from PEO into which Ni(II), Cd(II), Pb(II), Cu(II), Cu(I), and Mg(II) halide salts are dissolved. These electrolytes have a wide range of ionic conductivities and cation mobilities.

The principal focus of this work is on the effect of salt/polymer interactions, rather than that of gaseous oxygen, on the stability of the polymer. However, a consideration of the degradation of PEO electrolytes in the presence of oxygen may reveal useful information about how ions bind to PEO. For example, $CuCl_2$ greatly inhibits the oxidative degradation of PEG (MW 600),[12] while the same salt has no effect on the stability of PEG-M, which is the same as PEG except the chains are capped by methyl instead of hydroxyl groups. This shows how a salt may bind to certain groups more tightly than others.

Experiments were carried out in both nitrogen and air atmospheres using a combined thermogravimetry–mass spectroscopy (TG–MS) technique. Combined TG–MS has been used for some time to identify substances generated by polymer degradation.[13] TG–MS is different from a related technique, rapid pyrolysis–MS, in that TG–MS uses a heating ramp to decompose the specimen, whereas in rapid pyrolysis the sample is rapidly stepped to a single high temperature so that decomposition occurs isothermally. One advantage of a controlled rate of temperature

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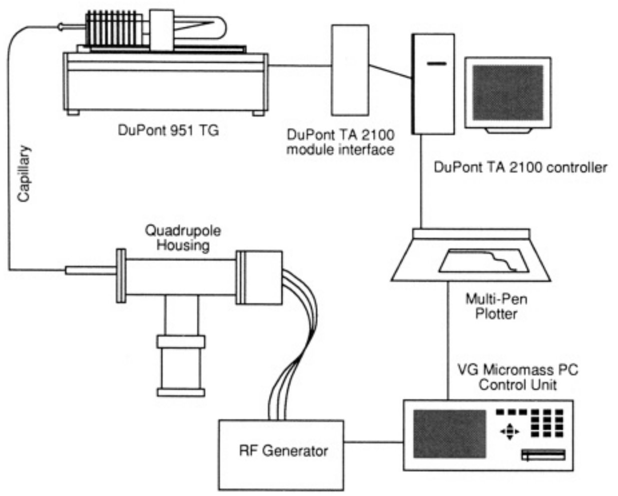

Figure 1. Schematic of equipment used for thermogravimetry–mass spectrometry.

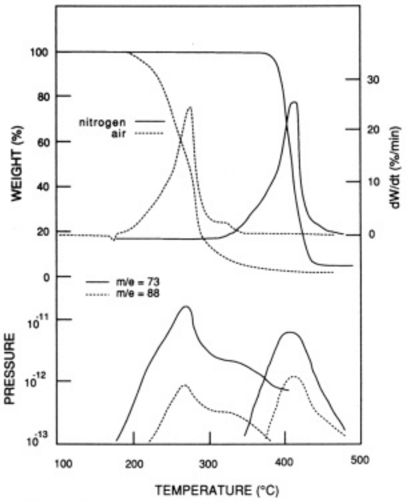

Figure 2. TG–MS of pure PEO (MW 5 × 10^6) under air and nitrogen at 10 °C/min.

rise is that separate decomposition steps can be distinguished more clearly than with the rapid pyrolysis technique. In addition, it is easier to understand the mechanisms when it is possible to identify the products seen in MS analysis with specific steps in the degradation process. A principal disadvantage of TG–MS is that (like most other MS techniques) secondary reactions may occur among the primary degradation products before detection.[14] Volatilized species may react in the TG cell, during passage from the TG to the mass spectrometer, or in the spectrometer itself. This must be considered, for example, when comparing mass spectra from decompositions at different temperatures.

Experimental Procedures

Polymer electrolyte samples were prepared by solution casting.[15] Appropriate amounts of PEO (Aldrich; MW 5 × 10^6) and salt (various suppliers, purity > 99.9%) were dissolved in suitable solvents. The solutions were stirred together and cast on a flat substrate to form films that were typically 100 μm thick. Electrolyte compositions are indicated in this paper in the style MX_2PEO_n, in which n is the number of PEO monomer units (also the number of ether oxygens) per cation. For example, $NiBr_2PEO_8$ would more correctly be written $NiBr_2(CH_2CH_2O)_8$. This convention ignores the polymer's molecular weight.

This work used a Du Pont 951 thermobalance with a Du Pont TA 2100 control system coupled to a VG Quadrupoles Micromass PC 300D mass spectrometer. A silica-lined stainless steel capillary, heated to about 175–200 °C, connected the heated chamber of the TG to the MS vacuum chamber. Since the capillary is also under reduced pressure, all low molecular weight compounds should be sufficiently volatile to allow passage to the detector, although some large polymer fragments may condense in the capillary. The equipment layout is shown schematically in Figure 1. The equipment and data collection procedures have been described in greater detail elsewhere.[16] Typically, samples weighing 10–20 mg were loaded into the TG, which was then flushed with dry air or inert gas. The samples were then heated at 10 °C/min under 100 mL/min of dry nitrogen or air, while the MS collected data continuously over the range 12–100 amu at 6 amu/s. The TG sample pan and quartz tube were cleaned after each run to remove sample residues.

Results

Decomposition of Pure PEO. Figure 2 shows the TG–MS of pure PEO under nitrogen and air. PEO degrades at much lower temperatures under oxygen than under nitrogen, although the mass spectra do not differ significantly. The mass spectra are similar to those obtained by Bortel,[4] Madorsky,[3] Grassie,[5] Costa,[8] and Taoda,[7] with pure PEO generating a large variety of products. We see higher levels of m/e 73 than m/e 88, behavior similar to the results of Lamot and Grassie, except that they both identified a major peak as methoxyacetaldehyde, which is m/e 74. Obviously, m/e 73 could be formed from a m/e 74 parent molecule by removing one hydrogen. We tested 1,3-dioxolane, which is essentially the cyclic isomer of methoxyacetaldehyde, and found the spectrum to be virtually identical with the that of PEO in the range 72–74 amu. In 1,3-dioxolane, this range corresponds to the parent peak mass (m/e 74) and the removal of one and two hydrogens (m/e 73 and 72) where m/e 73 is the major peak. We have previously found good agreement between the spectra of 1,4-dioxane and of PEO electrolytes in the range m/e = 80–90 amu,[10] which tends to support the current hypothesis that 1,4-dioxane is the species formed. In addition, Beynon et al.[17] have shown that aldehydes are more likely to fragment in the mass spectrometer but that m/e 73 is the major peak seen from 1,3-dioxolane. However, as we could not similarly test methoxyacetaldehyde, this conclusion is still tentative.

It is important to emphasize that we have not attempted to identify all the products evolved from the degradation of PEO and its electrolytes, since it is very difficult to distinguish among many isomers only with the use of mass spectrometry. This is especially true of PEO, which forms such a wide range of products. Whatever the true structures of species m/e 74 and 88 are, the levels of these fragments seem to be the most susceptible to different conditions, such as dissolved ionic salts, and are easily measured with the mass spectrometer. High molecular weight PEO also produces a condensable "cold ring" fraction, condensing in the TGA furnace tube, containing species much less volatile than these two. In addition, degradation under nitrogen appears to occur in one smooth step, while degradation under air may involve several steps. The stability of pure PEO depends on the purity of the inert atmosphere used for testing (Figure 3). Slower heating rates in standard-grade nitrogen (5 ppm oxygen) resulted in a small, sharp onset of weight loss that was qualitatively similar to that seen for samples run at higher heating rates in air. This onset was greatly reduced under a higher purity nitrogen (<1 ppm oxygen) at a slow heating rate and did not occur under regular nitrogen at faster heating rates. The onset was probably caused by traces of oxygen in the purge gas stream, which produced a small amount of oxidation. Oxidation, even in small amounts, produces hydroperoxides on the polymer chain that can

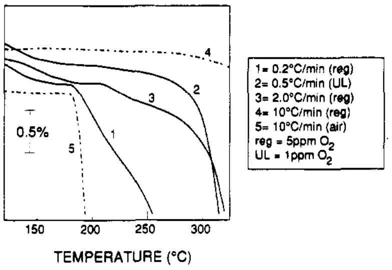

Figure 3. TG of PEO; heating rates and atmospheres as marked.

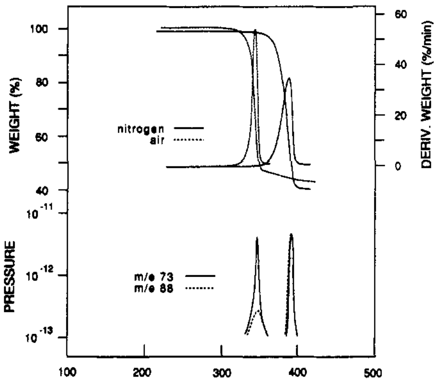

Figure 4. TG–MS of $NiBr_2PEO_8$ under air and nitrogen at 10 °C/min.

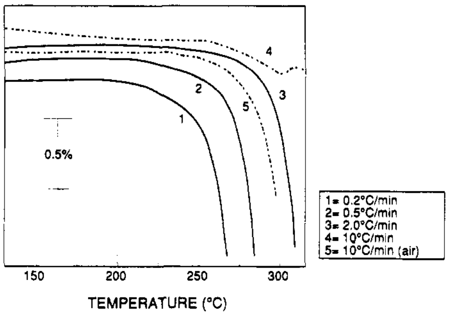

Figure 5. TG of $NiBr_2PEO_8$; heating rates and atmospheres as marked.

serve as initiators for subsequent degradation, as shown by the greater temperatures required for the onset to the final weight loss in the high-purity nitrogen run. However, traces of oxygen have little effect on the degradation products of PEO, just as the mass spectra were unaffected by air at higher heating rates.

Degradation of PEO-Based Electrolytes. $NiBr_2$-PEO_8: Figure 4 shows TG–MS data for $NiBr_2PEO_8$ under air and nitrogen. In nitrogen, $NiBr_2PEO_8$ is less stable than pure PEO and differs in the ratios of degradation products, with the amount of 1,4-dioxane (*m/e* 88) increased greatly. $NiBr_2PEO_8$ is only slightly less stable in air than in nitrogen, in sharp contrast to pure PEO which is greatly destabilized by air. However, in air the mass spectra for the degradation products of $NiBr_2PEO_8$ are very different from those taken under nitrogen (Figure 4). In both atmospheres the rate of weight loss (during degradation of the organic portion) is greater than with pure PEO. Also, $NiBr_2PEO_8$ produces much less cold ring fraction than does PEO, and the mass spectra signals are higher.

The reduced sensitivity of the degradation of $NiBr_2$-PEO_8 to the presence of oxygen is also reflected in Figure 5, which shows TG data recorded during slow heating under both high-purity and regular grades of nitrogen. With $NiBr_2PEO_8$ there is no early onset of weight loss as was

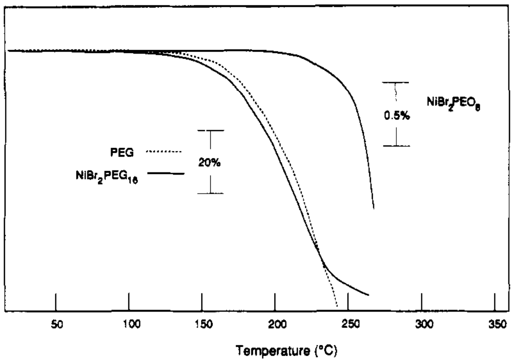

Figure 6. TG of PEG (MW 400) and $NiBr_2PEG_{16}$ under ultrapure nitrogen at 0.2 °C/min. Note the different weight loss scale for the high MW sample.

observed for PEO, which indicates that oxygen has a smaller effect on PEO containing $NiBr_2$. Transition metal ions are known to influence oxidative weight loss in polyethers by affecting the rates of both hydroperoxide formation and degradation.[9] Since the most influential variable affecting the observed degradation temperature of $NiBr_2PEO_8$ seems to be the heating rate and not the atmosphere, it appears that $NiBr_2$ interacts strongly with the PEO chains. Oxygen has a larger effect on the products of degradation (seen in the mass spectra) than on the stability, which could indicate that it is the products of secondary reactions that are being detected and not those directly formed upon electrolyte decomposition, although oxygen had no such effect on the spectra of PEO.

The $NiBr_2$–PEO system is also unusual in that it has two very different forms: "as-cast", with low conductivity and low Ni(II) mobility; and "modified", with much higher conductivity and Ni(II) mobility.[15] The results presented above are for as-cast materials, and there was little difference in results for modified samples. The modification procedure involves hydrating the as-cast films to an equilibrium composition containing about 30 water molecules/Ni(II) ion and then dehydrating the films at 140 °C under vacuum. The mechanism by which this procedure increases the ionic conductivity of the electrolyte is unknown. One possibility is that the presence of $NiBr_2$ might induce the decomposition of PEO into lower molecular weight fractions, since it is known that the conductivity of PEO electrolytes can be increased by the addition of PEG or PEG-M as a plasticizer.[18,19] Indeed, as measured by dilute-solution viscosity, there is an approximately 10-fold reduction in the average molecular weight when $NiBr_2PEO_8$ is modified. However, this indicates only that modification reduces the average molecular weight and not that it produces a large concentration of short-chain PEO.

If $NiBr_2$ did induce the formation of low molecular weight PEO, the fractions produced would have to have low volatility at 100–150 °C. Otherwise, their vaporization would show up as a weight loss during the heating of $NiBr_2$-PEO_8, and no such weight loss is observed. In fact, separate TGA experiments on pure PEG (MW 400) and PEG–$NiBr_2$ solutions (Figure 6) revealed that both samples lose weight quite rapidly at relatively low temperatures. These results suggest that no significant amount of short chain (MW ≤400) PEO fractions are formed in $NiBr_2PEO_8$, and other factors must account for the improved conductivity and ion mobility in its modified forms.

$PbBr_2PEO_8$, $CdBr_2PEO_8$: A previous paper[10] has reported that the stability of $PbBr_2PEO_8$ in air and nitrogen is very similar to that of PEO. Both $PbBr_2PEO_8$ and $CdBr_2PEO_8$ are almost as stable under nitrogen as

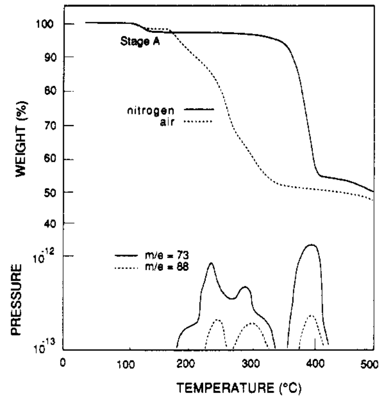

Figure 7. TG–MS $PbBr_2PEO_8$ of under air and nitrogen at 10 °C/min.

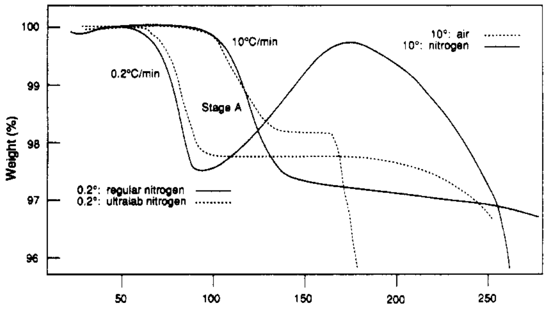

Figure 8. TG of stage A degradation of $PbBr_2PEO_8$; heating rates and atmospheres as marked.

PEO and produce similar mass spectra (see Figure 7 for $PbBr_2PEO_8$). Like PEO, both are much less stable in air than in nitrogen, and similar mass spectra are observed during degradation in each atmosphere. Figure 8 shows the onset of weight loss in $PbBr_2PEO_8$ during slow heating in regular and high-purity nitrogen. Like PEO, $PbBr_2PEO_8$ is destabilized by traces of oxygen in the purge gas stream but, unlike PEO, actually gains weight during oxidation. These electrolytes deposit cold ring fractions in similar amounts as PEO, and the mass spectra signals are also low.

One difference between these two electrolytes is the small initial weight loss observed only with $PbBr_2PEO_8$. For discussion, it has been identified as stage A degradation (Figures 7 and 8). It has been previously ascribed to either absorbed water or residual solvent, perhaps trapped in a crystalline phase.[20] $CdBr_2PEO_8$ exhibits no comparable weight loss. However, the weight loss is seen consistently in $PbBr_2PEO_8$ in various atmospheres and at different heating rates. At a higher heating rate (50 °C/min), traces of organics were observed in the mass spectra (1,4-dioxane, $m/e = 88$; CH_3Br, $m/e = 94, 96$). These results may indicate that a small amount of PEO chain degradation occurs during heating, that degradation occurs during sample preparation but chain rupture does not occur until heating, or that degradation occurs during sample preparation and the reaction products are trapped in the dried film.

The first explanation is unlikely since the weight loss in question does not recur upon subsequent heating[20] and is rate independent. If reactions were occurring during the heating, the extent of reaction should be influenced by heating rate and by isothermal experiments at the weight loss temperature, effects which were not seen. The other possibility is that the weight loss is the result of a one-time evolution of degradation products formed during the solution-casting process. It is well-known that, depending on the salt/solvent combination, PEO is sensitive to both oxidative and ion-catalyzed degradation while in solution[21] and may well decompose to small molecules containing acetyl or hydroxyl groups that are frequently formed upon the rupture or oxidation of polyether chains.[9,21] In addition, metal salts generally bond quite strongly to species such as acetyl and hydroxyl groups, so any small molecules could be held in the drying electrolyte film by metal salt interactions.

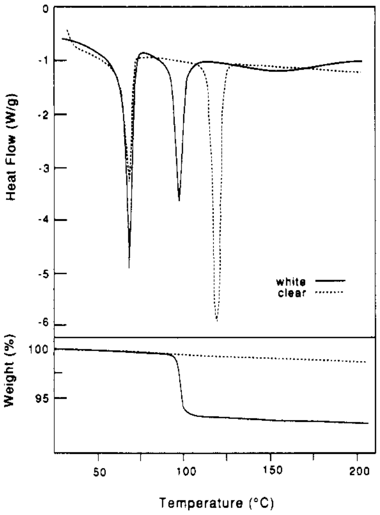

Figure 9. DSC and TG of two $PbBr_2PEO_8$ phases under nitrogen at 10 °C/min.

To explore these possibilities, $PbBr_2PEO_8$ was prepared by a different solution-casting scheme. Instead of casting from an acetonitrile–DMSO mixture, as previously, only DMF was used. The films formed in this way sometimes segregate macroscopically into equal amounts of two phases, one opaque white and the other clear and colorless. The white phase exhibits approximately twice the stage A weight loss as the original material, but the colorless phase loses no weight. Each forms a different high-melting PEO–$PbBr_2$ crystal complex phase, as seen by DSC (Figure 9), and the stage A like weight loss in the white phase coincides exactly with the endothermic DSC peak. On subsequent heating, DSC and TGA results for both phases appear identical. This means that the material evolved in the stage A weight loss was present before the TGA heating cycle and therefore must have been produced as separate molecules during the solution-casting process. Somehow this low molecular weight fraction is expelled by the formation of one of the crystal complex phases but not the other. Unfortunately, there is no ready explanation for why two such phases form and partition macroscopically or why the same or similar degradation occurs in two different solvent systems.

Further studies of the PbX_2–PEO family electrolytes revealed essentially the same degradation characteristics whether X was I or Br. TG–MS of PbI_2PEO_8 yielded nearly identical mass spectra as those of $PbBr_2PEO_8$ and very similar onsets of weight loss under air and regular-grade nitrogen.

$CuCl_2PEO_8$: The systems $[Cu(I)_zCu(II)_{1-z}X_{2-z}$ PEO_8 ($X = Cl^-, Br^-$) comprise another family of compositions that have different degradation characteristics from those of PEO. All CuX–PEO compositions exhibit multiple-step degradations, with the weight losses at lower temperatures occurring independently of atmosphere.[10] In $CuCl_2PEO_8$, traces of organic species were seen (1,4-dioxane) in the mass spectra during small weight losses that occurred only in the first heating cycle (Figure 10). The

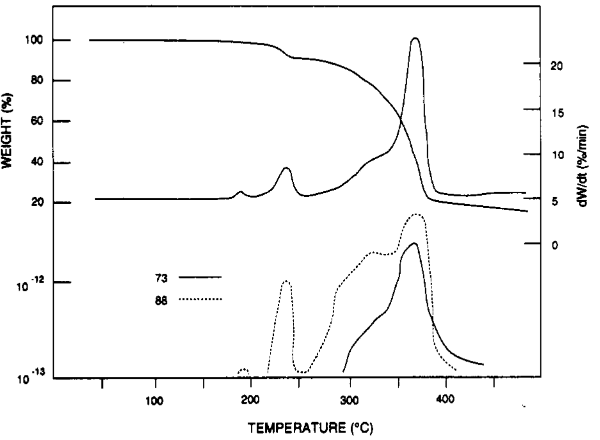

Figure 10. TG–MS of $CuCl_2PEO_8$ under nitrogen at 10 °C/min.

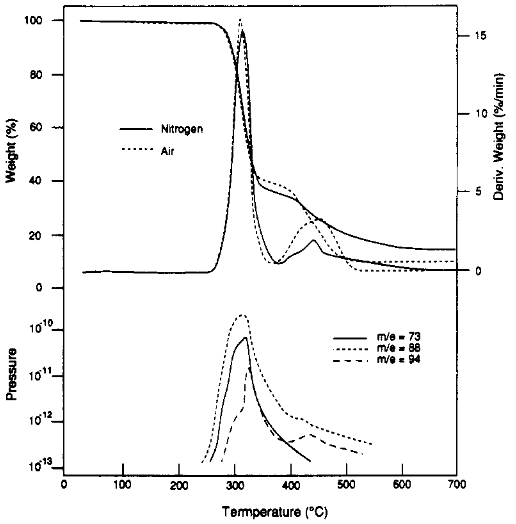

Figure 11. TG–MS of $MgBr_2PEO_8$ under nitrogen at 10 °C/min.

organic species are the same as those seen in the stage A degradation of $PbBr_2PEO_8$. Again, the "degradative" weight loss seems to be due to the loss of compounds formed during the casting process. Electrolytes containing mixed valences of Cu lose much more weight than those with nominally only one valence, which indicates that redox reactions may occur during solution casting. In general, it has been difficult to synthesize PEO electrolytes containing Cu salts and produce materials with reproducible properties, including weight loss curves. Often the size of the first and second weight losses varies from batch to batch. Since PEO is susceptible to solution degradation, and such degradation processes often have induction periods, variations in the time in solution might well alter the properties of the resulting films considerably. Note also that, in this family of materials, the choice of anion makes some difference in the thermal characteristics, which nevertheless are qualitatively very similar. Little cold ring fraction is formed by $CuCl_2PEO_8$, and mass spectra signals are higher than those in PEO.

MgX_2PEO_8: The final electrolytes studied here were $MgCl_2PEO_8$ and $MgBr_2PEO_8$, which have the distinction of being the least similar to PEO of all the systems studied (Figure 11, bromide only). The thermal behavior of these materials is remarkably unaffected by oxygen, and the mass spectra contain more m/e 88 than m/e 73. These electrolytes degrade at significantly lower temperatures than the others investigated here. Practically no cold ring fraction is formed by MgX_2PEO_8, and the mass spectral intensities are the highest of all the electrolytes studied to date. Other than the evolution of water absorbed by the films, which are very hygroscopic, there are no low-temperature weight losses observed with these electrolytes.

Relationship between Ionic Mobility and Electrolyte Degradation

It is reasonable to expect that the degradation pattern of a PEO-based electrolyte would be influenced by the strength of its ion/polymer interactions. Initial evidence suggests that with metal halide salts there is no significant anion effect on degradation, which is expected since halide anions should interact more weakly with the ether oxygen on the polymer chain than cations do. The more strongly a cation is associated with the polymer chains, the less mobile it is likely to be.

General indications of cationic mobility have been determined electrochemically for the electrolytes studied here.[15,20,22-27] Two cations that have very high ionic mobility are Pb(II) (in $PbBr_2PEO_8$)[19] and Cd(II) (in $CdBr_2PEO_8$)[22] These electrolytes have stabilities that are very similar to that of pure PEO. In contrast, Mg(II) is essentially immobile in MgX_2PEO_8,[23,24] and the stability of this electrolyte is quite different from that of PEO in both air and nitrogen. These observations would suggest that when cations are mobile, their interactions with PEO are such that they do not exert a strong influence on the degradation of the polymer. The amount of cation/polymer interaction is related to an electrolyte's overall conductivity, since electrolytes with high cation mobility usually have lower overall conductivity. It is reasonable to conjecture that extensive cation/anion aggregation occurs in electrolytes with high cation mobility, which reduces the ionic conductivity, while in electrolytes with low cation mobility the cations interact so strongly with the polymer that the anions are free to move and achieve higher conductivity.

The amount of "cold ring" fraction, or condensable degradation products, formed by each system also correlates in much the same way. Systems like PEO that have large amounts of condensables ($PbBr_2PEO_8$, $CdBr_2PEO_8$) have the least cation/polymer interactions, and the system with the least condensables, MgX_2PEO_8, has the most cation/polymer interactions.

However, this correlation is not completely general. Members of the CuX_z family of electrolytes, in which cations appear to be mobile,[25-27] do not appear to degrade like PEO. Recent results[28] indicate, however, that in the presence of CuX_z salts PEO undergoes degradation during the solution-casting process to a much greater extent than do the other electrolytes studied here. At least in the equipment used in this study, degradation of low molecular weight PEO yields spectra containing more m/e 88, which could account for the high yield of m/e 88 observed from electrolytes containing copper salts. In addition, PEO that has partially degraded in solution would presumably degrade at lower temperatures, leaving any high molecular weight species to be degraded in the presence of a higher salt concentration. Degradation of pure PEO could explain why the level of m/e 73 increases in the last step of weight loss, although the level is not as high as that observed in pure PEO since the salt concentration is higher.

$NiBr_2PEO_8$ is also an unusual case since it exhibits both high and low cationic mobility, depending on the details of electrolyte preparation.[15] However, both forms degrade at similar temperatures, produce similar mass spectra, and are rather unaffected by oxygen. We currently have no explanation for this phenomenon although there is evidence that $NiBr_2$ precipitates above 200 °C. However, if $NiBr_2$ precipitates, one would expect PEO to degrade in the normal manner.

Conclusions

The stability of poly(ethylene oxide) is strongly influenced by oxygen and various dissolved metal salts. The degradation of PEO, $PbBr_2PEO_8$, and $CdBr_2PEO_8$ is readily initiated by even the slight traces of oxygen found in standard-grade "inert" gases. Pb(II) and Cd(II) halide salts have litte effect on the stability of PEO and also have high cationic mobility. In contrast, immobile cations like Mg(II) strongly influence the stability of PEO. The choice of halide anion makes a much smaller difference in stability than the choice of the cation. Since the salt may be consumed during degradation—either by precipitation or formation of salt/polymer covalent bonds—the salt cannot necessarily be considered as catalysts in these electrolytes. Finally, it appears that certain electrolytes are degraded by the solution-casting procedure, which can alter the bulk degradation behavior, but the effect of such degradation on conductivity and other properties is not known.

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Registry No. PEO, 25322-68-3; $NiBr_2$, 13462-88-9; $PbBr_2$, 10031-22-8; $CdBr_2$, 7789-42-6; $CuCl_2$, 7447-39-4; $MgBr_2$, 7789-48-2; $MgCl_2$, 7786-30-3.