Thermal and Thermooxidative Degradation of Poly(ethylene oxide)–Metal Salt Complexes

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Received March 3, 1992; Revised Manuscript Received June 1, 1992

ABSTRACT: Thermal and thermooxidative degradation studies of electrolytes based on poly(ethylene oxide) (PEO) have been extended to include a range of inorganic salts to elucidate the role of the salt. In confirmation of earlier studies, inorganic salts generally reduce the thermal stability of PEO in an inert atmosphere but protect the polymer against thermal oxidation. These effects are explained, in part, by the strength of the interaction between the metal cation M^+ and the oxygen atoms in the polymer backbone. The greater the charge density of M^+, the greater its destabilizing influence during degradation under nitrogen and the greater its stabilizing effect in an oxidizing atmosphere. This arises because complexation tends to reduce the strength of backbone C–O bonds but also retards peroxidation at adjacent C–H bonds. The anions also influence the decomposition reactions both by screening the cations and by direct chemical interaction. In the presence of oxygen, acetaldehyde, methanol, and CO_2 are the most abundant low-boiling products from both PEO and its complexes. Ethylene, which is abundant when PEO–salt complexes are pyrolyzed under N_2, is absent. Methyl and ethyl formates are also formed in small amounts from complexes but not from pure PEO, though the latter does evolve small amounts of other esters and dioxane. Mechanisms of thermooxidative degradation accounting for these observations are proposed.

Introduction

Detailed studies of the physicochemical properties of polymer electrolytes based on poly(ethylene oxide) (PEO)[1] have been extended recently to include their thermal and thermooxidative stability.[2,3] The latter investigations have shown that the decomposition pattern of the PEO is highly sensitive to the nature and concentration of the dissolved salt during pyrolysis in both air and nitrogen. Most of our early work involved the salts NaSCN and $LiClO_4$, the former being mildly reducing and the latter strongly oxidizing in nature. In an inert atmosphere both salts reduce the thermal stability of PEO, the destabilizing influence of $LiClO_4$ leading to almost explosive decomposition at ca. 320 °C, that is, about 80 °C below the degradation threshold of pure PEO or the thiocyanate complex. In air, pure PEO and its complexes with NaSCN and $LiClO_4$ are less thermally stable than in N_2 but there is a remarkable change in the relative stabilities of these materials—pure PEO is the least and the NaSCN complex the most stable. But the most surprising observation is that the $LiClO_4$ complex is more stable in air than is pure PEO (though, once initiated, the decomposition of the perchlorate complex is very rapid).[3]

Thus, it appears that in an oxidizing atmosphere dissolved salts exert a stabilizing influence on PEO. This is supported by spectroscopic evidence which suggests that these dissolved salts retard the thermal oxidation of PEO.[3]

To throw further light on the mechanism of the action of salts on the thermal and thermooxidative degradation of PEO, we have extended our studies to include a wider range of inorganic salts. We have also completed an investigation of the volatile products of thermooxidative degradation of PEO–salt complexes for comparison with our previously published data concerning degradation under N_2.[2] The results of these studies are reported in this paper.

Experimental Section

The PEO (BDH, nominal MW 6 × 10^5) was the material employed in our earlier work.[2,3] Complexes were prepared as before by cosolution of the salts (MX) and polymer in dry acetonitrile or methanol. The solvent was removed by rotary evaporation followed by high vacuum pumping for several days. The concentration of salt is expressed as the molar ratio, [EO]/[M], of monomeric unit to salt.

Thermogravimetry, both dynamic (linear heating at 10 °C min^{-1}) and isothermal, was conducted in a Du Pont 951 thermogravimetric analyzer controlled by a 1090 thermal analyzer unit. The atmosphere was a current of air or nitrogen as desired (60 mL min^{-1}), and the sample weight was 10 mg.

The volatile products of thermooxidative degradation from dynamic thermogravimetry were collected in a U-trap cooled to −80 °C and identified by the HRGC–FTIR technique.

Results and Discussion

Degradation in N_2. Figures 1 and 2 show that on heating under N_2, the stability of the complexes is in the order PEO–LiCl > PEO–KI > pure PEO > PEO–KSCN > PEO–$MgCl_2$ > PEO–LiSCN > PEO–LiI. A multistep degradation process is induced by $MgCl_2$ whereas in the case of the other salts, thermal volatilization of PEO occurs in a single step, as when it is pure. The larger residue left by the complexes, as compared to pure PEO at 500 °C, is due both to products from the salt and increased charring of PEO.

In a previous paper[3] we proposed that complexation of the cation M^+ with the oxygen atoms of the PEO backbone destabilizes the polymer by weakening the adjacent C–O bonds. It is widely accepted that M^+–oxygen atom interaction plays a key role in the formation of complexes of polyethers and metal salts. In the case of poly(propylene oxide) (PPO), strong interactions between the metal ion of the complexed salt and the backbone oxygen atoms

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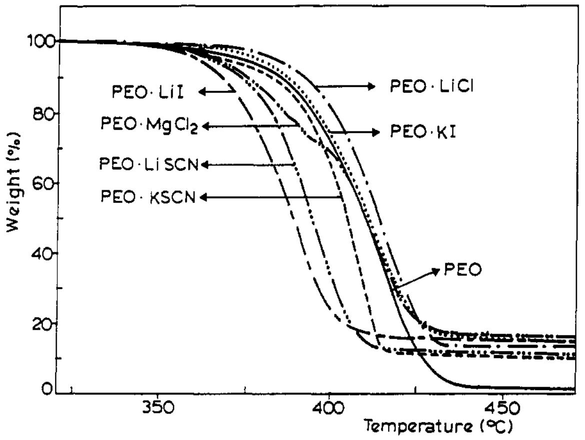


Figure 1. Thermogravimetry (TG) curves of PEO and PEO–salt complexes (molar ratio of monomeric [EO]/[salt] = 32:1). Sample weight, 10 mg; atmosphere, N_2, 60 mL min^{-1}.

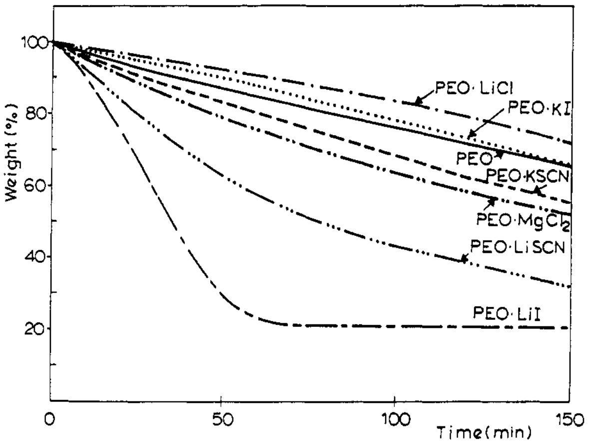
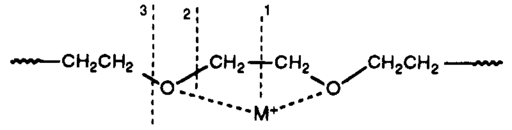


Figure 2. Isothermal mass changes under N_2 at 322 °C of materials in Figure 1.

are revealed in the IR absorption spectrum of the polymer.[4,5] Other, though less direct, evidence of such interactions comes from the increase in the glass transition temperature T_g of PPO on complexation with salts.[6,7] It is more difficult to obtain direct spectral and other evidence for M^+–oxygen interactions in the case of PEO because of crystallinity of the polymer and its complexes.[8] Nevertheless, it is difficult to account for the remarkable complexing powers of PEO for metal salts without invoking a strong interaction between the metal ion and the oxygen atoms of the polymer.[9] We propose that because of the M^+–oxygen interaction, bonds 2 and 3 undergo thermal scission at a lower temperature in the metal complex than in pure PEO where they have a bond energy comparable to the C–C bond 1. Therefore, complexation of PEO with metal salt leads to an increase in the ratio of C_2 $\sim\!\sim$–$OCH_2\dot{C}H_2$ over C_1 $\sim\!\sim$–$O\dot{C}H_2$ terminated macroradicals during thermal degradation and so alters the nature of the degradation products.[2,3]



If this explanation is correct, the destabilizing influence of the M^+ cation should increase with increasing strength of the interaction between M^+ and the oxygen lone pair electrons. Thus, the greater the charge density, or more correctly the polarizing power of the cation, the greater should be its destabilizing influence. The polarizing powers (relative to Li^+) of the cations involved in this study are Mg^{2+}, 1.3; Li^+, 1.0; and K^+, 0.73.[10] The relative destabilizing influence of these cations also follows this order. Thus, relative thermal stabilities of pairs of complexes with a common anion are PEO–$MgCl_2$ < PEO–LiCl, PEO–LiI < PEO–KI, and PEO–LiSCN < PEO–KSCN. This order of instability also follows the strength of the cation–oxygen interaction in PPO as evidenced by IR band shifts and changes in T_gs.[5-7]

The above cation–oxygen interaction accounts for the relative thermal stability of complexes of salts of the same anion and different cation but does not explain the effect of the anions. Indeed, the difference in thermal stability between complexes of salts of the same cation and different anion (e.g., LiI and LiCl) can be comparable to that observed when the cation is changed (e.g., LiI and KI).

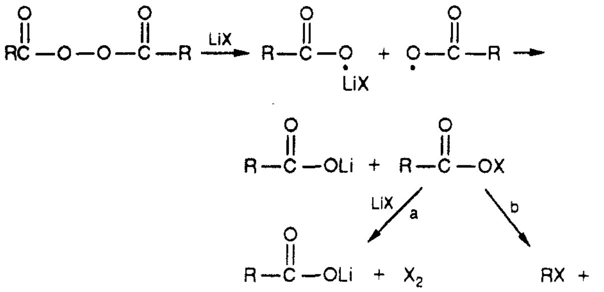
Effects of the anion on the T_g of PPO–salt complexes have also been observed previously and attributed to modification of cation–oxygen interaction due either to the screening effect on the cation by the anion or to a combination of "size" (sum of anion and cation radii) of the salt and the ionic character of the metal–anion bond.[6] These effects are likely to play a role in the relative thermal stability of PEO complexes. For example, if we assume that I^- is characterized by a lower screening power than Cl^- because of its lower charge density, then the interaction Li^+–oxygen should be stronger in the LiI complex than in the LiCl complex. The former should therefore be less stable, as indeed is observed experimentally (Figures 1 and 2). Furthermore, the lower destabilization by $MgCl_2$ as compared to LiI, despite the polarizing power of Mg^{2+} being 1.3 times that of Li^+, can be explained by the much more effective screening action of Cl^- as compared to I^-.

While the screening effects of the anions moderate the destabilizing influence of the cation by regulating the strength of its interaction with oxygen atoms, they do not account for the thermal stabilization of PEO observed, for example, in complexes with LiCl or KI (see Figure 2). Chemical interactions must also take place between the salt and the polymer. Thus, we reported previously that the thiocyanate group undergoes reaction on heating PEO–NaSCN complexes to 500 °C in nitrogen, whereas NaSCN is stable when heated alone in the same conditions.[2] Similarly, violet fumes, probably I_2, are evolved on heating PEO–LiI complexes, whereas LiI is thermally stable to 500 °C. It seems probable that these reactions involve the salt and the radicals which propagate the decomposition of PEO.[3] Examples are reported in the literature of redox reactions between alkyl radicals R and metal ions, leading to carbonium ion formation[11,12]

$$M^{n+} + R \rightarrow M^{(n-1)+} + R^+ \qquad (1)$$

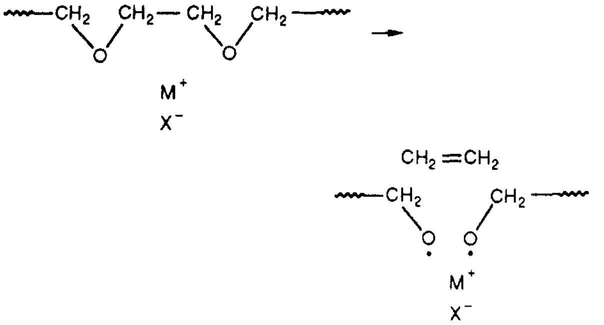
which might act as a termination step in the radical degradation process. Reaction 1 might be favored in the present case when the salts are truly dissolved (as opposed to simply dispersed) in the polymer, leading to close contact between metal ion and free radical centers. Literature data show that the occurrence of reaction 1 depends on the type of cation, concentration, and temperature. However, there are no reports of this type of reaction involving alkali metal or alkaline-earth ions.[11,12]

Free radicals generated by peroxides react with metal halides (e.g., LiBr, LiCl) as follows:[13,14]



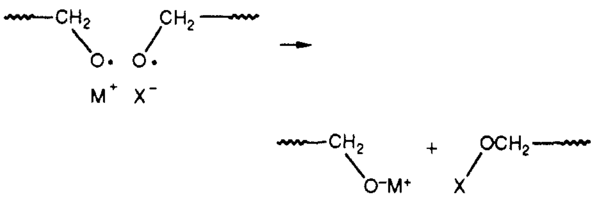
(2)

A similar reaction can occur with alkali metal thiocyanates.[15] During the thermal degradation of PEO–salt complexes, the large amounts of evolved ethylene[2] may originate from scission of adjacent C–O bonds:



(3)

The alkoxy radicals generated by ethylene elimination in (3), like the radicals generated by peroxide decomposition in (2), are in close proximity to the metal salt. If reaction 3 were to continue along the route shown for reaction 2, the radical termination process



(4)

would occur. The nucleophilic reactivity of the halogen ion controls the reactivity of lithium halides in reaction 2, which in turn seems to depend on ion pair formation. Reaction 4, if it occurred, would tend to decrease the rate of degradation of PEO complexes, but it is not easy to predict whether the rate could be lower than that of pure PEO.

Summarizing, the metal–oxygen interaction in PEO–salt complexes tends to destabilize PEO by weakening the adjacent C–O bond. However, it seems that this effect can be partially offset or even overwhelmed by stabilizing chemical interactions involving the radicals which propagate the degradation of PEO and the metal ion or the anion or both ions.

Thermal Oxidation. The thermal decomposition of PEO is very sensitive to the action of oxygen. Thus, heating in nitrogen at 10 °C min^{-1} gives 50% volatilization at 410 °C (Figure 1), whereas for the same heating rate in air the temperature for the same level of decomposition is lower by about 100 °C (Figure 3). The temperature of degradation of the PEO complexes is also lowered in the presence of oxygen although the effect is less marked than for pure PEO. For example, for the PEO–LiCl complex, where the effect of oxygen is greatest, the corresponding temperature difference at 50% weight loss is 75 °C (Figures 1 and 3). The partial protection of PEO against the action of oxygen afforded by complexed salt is clearly evident when the rates of volatilization of the complexes and pure PEO heated in air are compared (Figures 3 and 4).

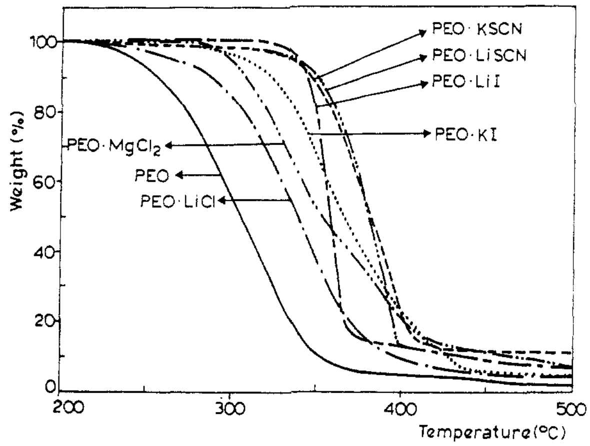


Figure 3. TG in air (60 mL min^{-1}) of materials in Figure 1.

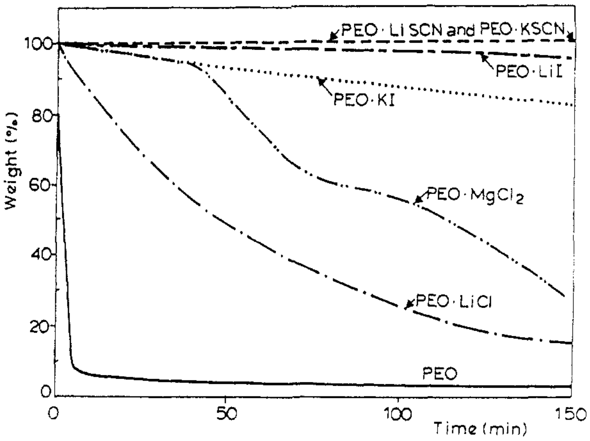


Figure 4. Isothermal mass changes under air at 322 °C of materials in Figure 1.

The extent of protection depends on the type of salt, the effectiveness increasing in the order LiCl < $MgCl_2$ < KI < LiI < LiSCN ≃ KSCN. The complexed salt appears to reduce the rate of thermal oxidation of PEO without otherwise altering the reaction. However, in the case of LiI, although the onset of weight loss of the complex occurs at a higher temperature compared with pure PEO, the rate of weight loss is markedly greater (see Figure 3). Furthermore, the PEO–$MgCl_2$ complex decomposes by at least two steps compared to the single step in the thermogram of the pure PEO. A similar effect was observed in the thermal degradation in nitrogen.

Acetaldehyde and methanol are the most abundant low-boiling products of thermooxidation of PEO, whether or not complexed salt is present (Table I). Carbon dioxide is also present in significant amounts but could not be quantified exactly with our experimental setup. Small amounts of dioxane and esters (except for alkyl formates) are also evolved from pure PEO. However, methyl and ethyl formates are typical products formed in small amounts by thermal oxidation of complexes (e.g., PEO–LiI, Table I), and other compounds may also be evolved during thermal oxidation depending on the type of salt (e.g., HCN from thiocyanates, Table I).

With respect to chemical changes that occur in the polymer during thermal oxidation there is a marked difference between pure PEO and its complexes. In the case of pure PEO, absorptions at 3470 (OH stretch), 1740 (C=O ester stretch), and 1725 and 1183 cm^{-1} (C=O and C–O stretching, respectively, in alkyl formates) develop during thermal oxidation (Figure 5B). In the case of the

Table I
Low-Boiling Products of Thermal Oxidation of PEO and PEO-Salt Complexes Heated in Air at 10 °C min^{-1} to 500 °C

	CO_2	CH_3CHO	CH_3OH	$HCOOCH_3$	$HCOOC_2H_5$	dioxane	esters
PEO	P[a]	+++++	+++	–	–	+	++
PEO-LiI	P	++++	+++	+	+	+	
PEO-NaSCN	P	++++	++		+		+ [+HCN]
PEO-LiCl	P	++++	++				+

[a] P = present.

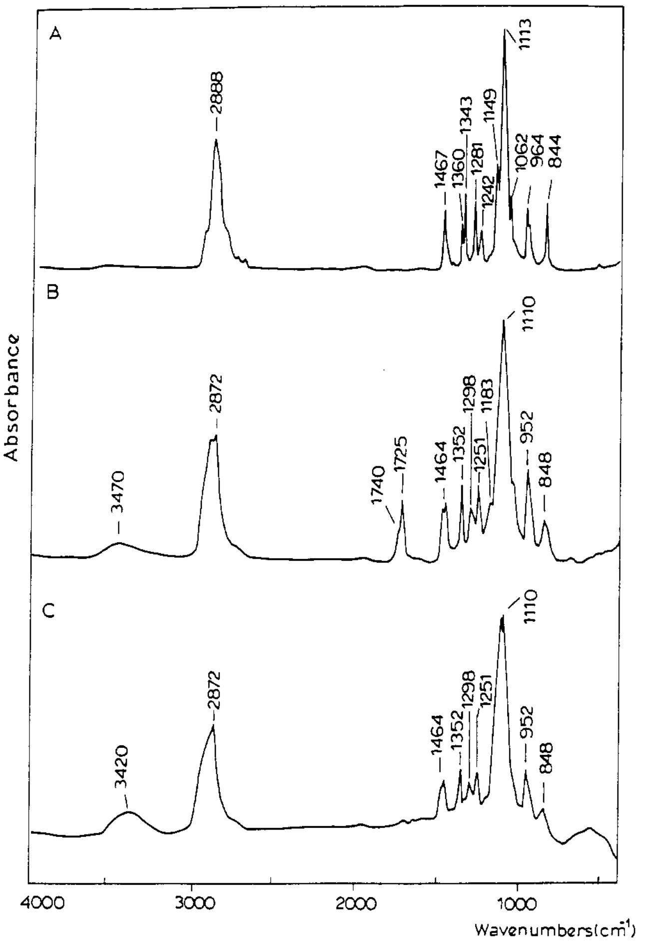


Figure 5. IR spectra of (A) pure unoxidized PEO, (B) pure PEO heated in air at 150 °C for 200 min (weight loss 15%) and (C) PEO-LiCl complex ([EO]/[salt] = 32:1) heated in air at 200 °C for 200 min (weight loss 25%). Air flow, 60 mL min^{-1} in B and C.

complexes, only the absorption due to OH (3420 cm^{-1}) and a very weak ester absorption (1740 cm^{-1}) are evident (Figure 5C), while there is no indication of formation of alkyl formate groups. [Note: some of the IR data quoted here differ slightly from those in ref 3. The data here are more accurate.]

Mechanism of Oxidation. The key role of secondary hydroperoxides (I in Scheme I) in the photooxidation or thermal oxidation of PEO has been demonstrated.[16] The thermal decomposition of the hydroperoxide groups (reaction a, Scheme I) gives a hydroxy and an alkoxy radical (II), which may further react following reactions b–e of Scheme I. The IR spectrum of the oxidized polymer indicates a high concentration of formate groups but a low level of other ester groups and no aldehydes (the H–COR stretching at 2740 cm^{-1} is absent (Figure 5B)). These observations indicate that β scission of the alkoxy radical (reaction e, Scheme I) is more likely and that route d (β_1 scission) is negligible. A similar result was found in the case of photo-[16] and radiation-induced[17,18] oxidation of PEO. In particular, as was previously underlined,[16] the β_2 scission takes place in alkoxy radical II despite the fact that β_1 scission, since it involves a C–O bond, is characterized by a lower energy (by 3 kcal mol^{-1}) than β_2 scission, which involves a C–C bond.

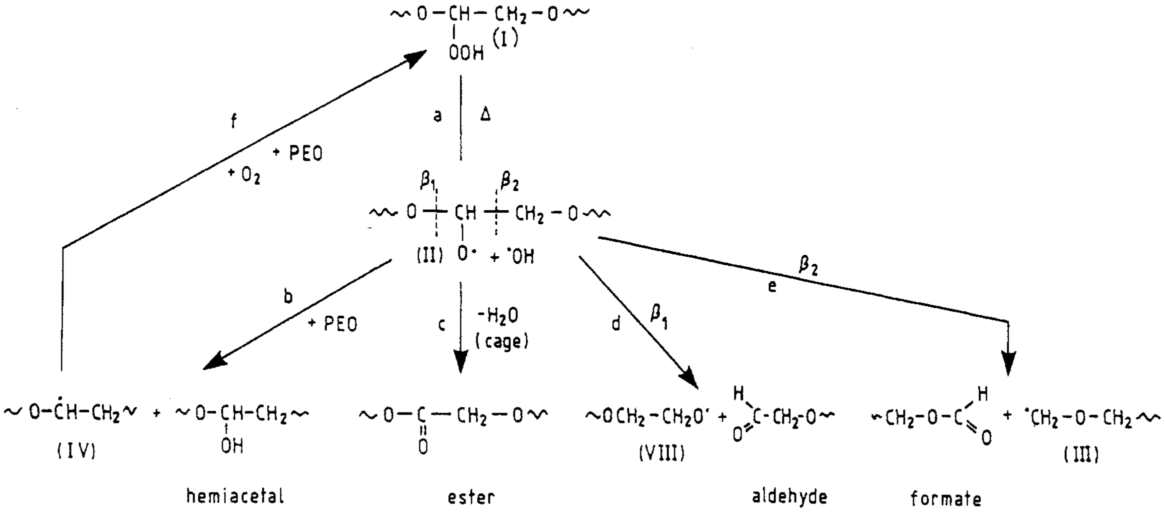
The probability of reaction b, leading to hemiacetal, is not easy to establish because OH groups are also introduced in the polymer through other reactions (see below, Scheme II).

The formation of the low-boiling volatile products (CO_2, CH_3CHO, CH_3OH) which we have identified in the thermal oxidation of PEO can be derived as in Scheme II, for example, by thermal or thermal oxidative reactions of the formates and macroradical III created by the route a + e of Scheme I, the favored reaction path for hydroperoxides. Formates are likely to be a major source of H atoms in abstraction processes from peroxy or alkoxy radicals propagating the oxidation process (Schemes I and II). Indeed, the H atom of formates is the most extractable atom present in the system, being comparable to that in aldehydes, which is thought to be among the most reactive[19] (the difference in activation energy between formates and aldehydes for H abstraction is 1–2 kcal mol^{-1}).[20] The resulting acyl radical V should undergo rapid elimination of CO_2 (reaction 2, Scheme II), a more favorable reaction than elimination of CO,[20] with formation of the primary alkyl radical VI. This radical might be a direct source of CH_3CHO by γ scission, implying 1,2 H transfer to form a more stable secondary radical VII which then undergoes β scission (reactions 3 and 4, Scheme II). The chain character of this process, propagated by reactions 3 and 4 of Scheme II, is in agreement with CH_3CHO being the major volatile product of thermal oxidation of PEO.

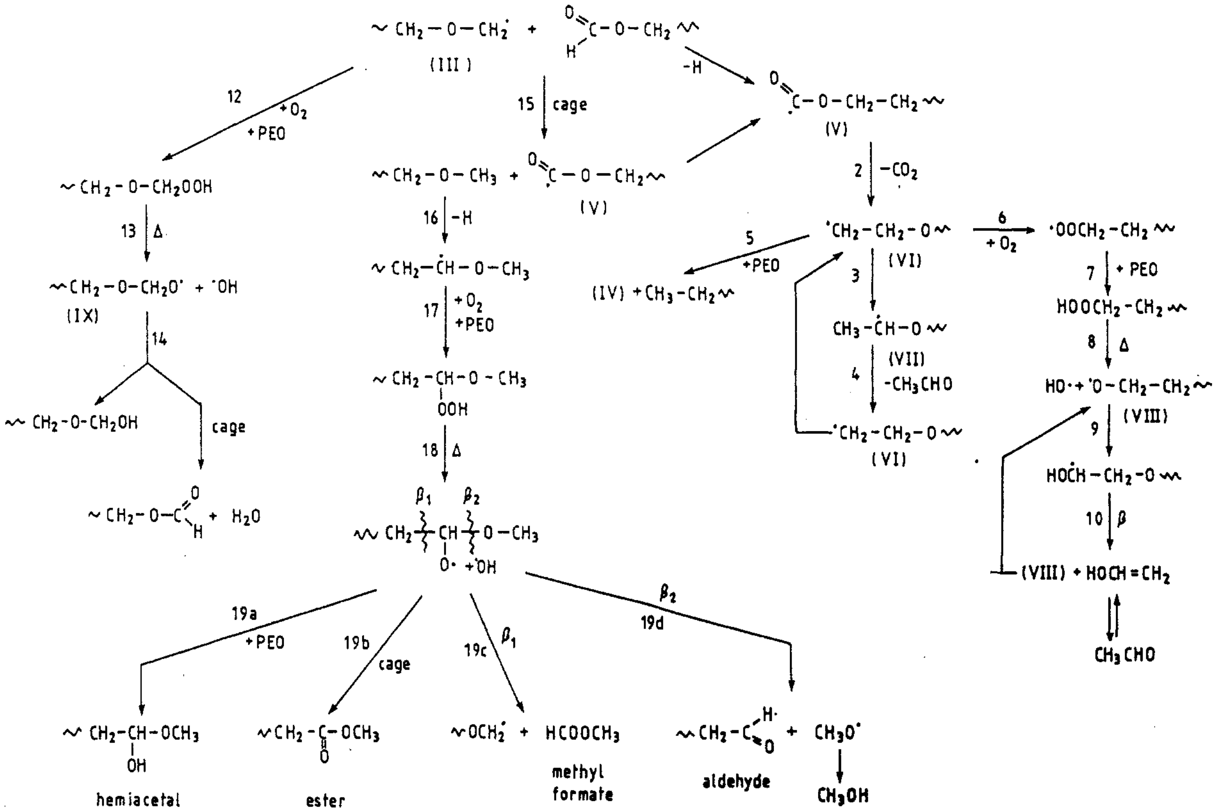
However, one would expect reactions 3 and 4 to compete with direct β scission of radical VI to produce ethylene (as occurs in purely thermal degradation of PEO complexes[3]). Since ethylene is absent from the products of thermal oxidation of PEO and its complexes, a more probable reaction route for radical VI is oxidation (reaction 6, Scheme II). Further reaction of the peroxy radical through steps 7–10 of Scheme II would lead to vinyl alcohol formation from the alkoxy radical VIII through rearrangement and β scission. Vinyl alcohol would rapidly rearrange to acetaldehyde. This route to acetaldehyde has similar chain characteristics (propagation reactions 9 and 10) to that discussed above for the alkyl radical VI. The process could be terminated by coupling or disproportionation of radical VI or by H transfer to radicals VI or VIII, for example, from CH_2 groups of the polymer or from formate groups.

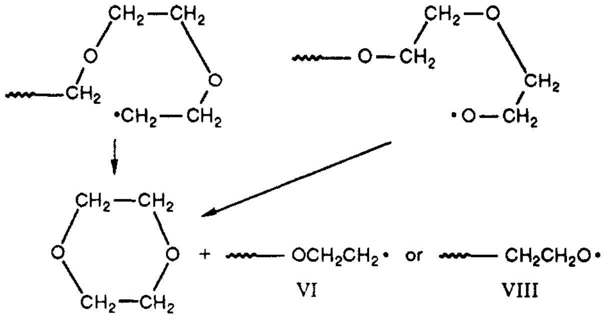
Dioxane, which was found in small amounts in the thermal oxidation of PEO, might be formed by cyclization, which occurs less frequently than γ scission, of radicals VI or VIII:

Scheme I
Thermal Oxidation of PEO: Primary Products



Scheme II
Thermal Oxidation of PEO: Secondary Products





(5)

Radical III, which is formed simultaneously with formates, does not apparently undergo β scission, because the product CH_2O of this step is not present in the volatile degradation products. On the other hand, CH_2O is formed during oxidation of PEO initiated by γ-ray irradiation at 25 °C, its production being proposed to occur through β scission of radical III.[17,18] Therefore, we assume that at the temperatures used in this work, radical III either reacts with oxygen (reaction 12, Scheme II), abstracts hydrogen for example in a "cage" as in reaction 15,[17] or terminates by coupling. In the case of oxidation (reaction 12, Scheme II), the resulting hydroperoxide is likely to decompose in a cage, giving a formate group because of the highly mobile H atom between two oxygen atoms in the alkoxy radical IX. Conversion of radical III to formate, which would react further as discussed earlier, would therefore occur.

In the case of H transfer to radical III (reaction 15, Scheme II), methoxy chain end groups would be formed. Oxidation of the end groups (reactions 16–19) would account for the formation of methanol and methyl formate, neither of which would be obtained from any reaction discussed so far. Methanol was, however, found in amounts comparable to that of acetaldehyde. Therefore, if methanol is formed via oxidation route 16–19, large amounts of aldehydes should also be found in the oxidizing polymer. This was not observed.

Several considerations lead us to suggest that methanol is formed by oxidation of part of the CH_3CHO evolving from oxidizing the PEO:

1. The reaction

$$CH_3CHO + O_2 \rightarrow CH_3OH + CO_2 \qquad (6)$$

is energetically favored by ca. 100 kcal mol^{-1}.

2. Acetaldehyde is formed in the thermal and thermooxidative degradation of PEO (this work and ref 3), PPO, and PTHF,[21] but methanol is only formed on heating these polymers in the presence of oxygen.

3. Both acetaldehyde and methanol are formed in parallel in the thermooxidative degradation of polyethylene[22] and polypropylene,[23] in which there is no oxygen source within the polymer structure.

4. In the thermooxidative degradation of the PPO–LiI complex, where CH_3CHO formation is minimal, CH_3OH formation is also minimal.[21]

5. We note that CH_3CHO is produced in the photooxidation of PPO at ambient temperature but CH_3OH is absent.[21]

Thus, it appears that CH_3OH is a product of thermal breakdown of CH_3CHO in an oxygen-containing atmosphere at temperatures above 200 °C and in the presence of radicals. Reaction 6 has been postulated previously to explain the formation of the methanol in the case of the thermal oxidation of polypropylene.[23]

Oxidation of CH_3CHO diffusing through the oxidizing PEO might be initiated by abstraction of its very mobile H atom by peroxy radicals of the polymer:

$$POO^{\bullet} + CH_3CHO \rightarrow CH_3CO^{\bullet} + POOH \qquad (7)$$

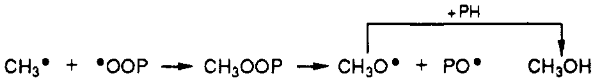
The radical $CH_3CO^{\bullet}$ is reported to decompose above 200 °C to give CO and a methyl radical[20]

$$CH_3CO^{\bullet} \rightarrow CH_3^{\bullet} + CO \qquad (8)$$

which could react with oxygen, producing methanol through the well-known oxidation mechanism

$$CH_3^{\bullet} + O_2 \rightarrow CH_3OO^{\bullet} \xrightarrow{+PH} CH_3OOH \xrightarrow{\Delta} CH_3O^{\bullet} + {}^{\bullet}OH \xrightarrow{+PH} CH_3OH \qquad (9)$$

An alternative route to methanol from methyl radicals involves reaction with peroxy radicals in the system:



$$\begin{tikzcd} CH_3^{\bullet} + {}^{\bullet}OOP \arrow[r] & CH_3OOP \arrow[r] & CH_3O^{\bullet} \arrow[rr, bend left, "+PH"] & + PO^{\bullet} & CH_3OH \end{tikzcd} \qquad (10)$$

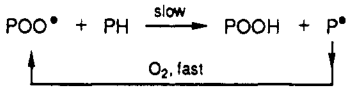
Reactions 8 and 9 for CH_3CHO oxidation to CH_3OH imply evolution of CO in an amount comparable to that of CH_3OH. This point requires confirmation because CO does not condense under the conditions we used to collect the volatile degradation products.

In Scheme II reaction 19c is a possible route to $HCOOCH_3$ as an alternative to CH_3OH. The same sequence of reactions can produce $HCOOC_2H_5$ if ethoxy groups (formed, for example, by H transfer to radical VI) are involved instead of methoxy groups. Both methyl formate and ethyl formate have been detected in the thermooxidative degradation of PEO complexes (Table I).

The lack of formaldehyde in the volatile products of degradation is somewhat surprising since CH_2O could be formed not only from III but by β scission of the radical $OCH_2CH_2O^{\bullet}$ (VIII). However, this radical would seem the most likely source of CH_3CHO either by direct γ scission or after formation of CH_2CHOH via hydrogen transfer, followed by β scission (reactions 9 and 10, Scheme II).

Mechanism of Stabilization of PEO in Complexes. The apparent absence of carbonyl groups, essentially formates, in the polymer during oxidative degradation of PEO complexes is the major difference between the chemistry of pure PEO and that of its complexes with inorganic salts (see Figure 5). The formation of carbonyl groups in the complexes is indicated by the nature of the low-boiling products of oxidation which are derived essentially from formates and which are very similar in the cases of pure PEO and its complexes. The formates might not accumulate in the polymer to a detectable concentration in the complexes because they are produced at a rate lower than or comparable to that of decomposition, while the reverse prevails in pure PEO.

These considerations bring us to discuss the formation and decomposition of hydroperoxides in PEO complexes because they are the source of formates. A lower rate of hydroperoxide formation in the PEO complexes, as compared to the parent polymer, would account for our results. The rate-determining step in the radical process leading to hydroperoxides is the hydrogen abstraction by peroxy radicals:



$$\begin{tikzcd} POO^{\bullet} + PH \arrow[r, "slow"] & POOH + P^{\bullet} \arrow[l, bend left, "O_2,\ fast"] \end{tikzcd} \qquad (11)$$

It seems probable that the metal–oxygen interaction which weakens the adjacent C–O bond, as discussed above, simultaneously reduces the reactivity of neighboring methylene groups by diminishing the capacity of the interacting O to delocalize the radical formed upon H abstraction. The effect of metal–oxygen interaction on the strength of neighboring C–H bonds is observed in the shifts of C–H stretching bands in the IR spectra of PPO–alkali metal thiocyanate complexes.[5] If hydroperoxide formation in the complexes is retarded in this manner, then those salts which have the greatest *destabilizing* effect in degradation under nitrogen should have the greatest *stabilizing* influence in air. Thus, in broad terms, we should expect LiCl to have the smallest stabilizing influence in air and LiI the greatest—quite close to what is shown in Figure 4. (The slightly more effective stabilizing influence of the thiocyanates will be discussed later.) If we compare the order of stabilizing power against thermal oxidation of PEO complexes of salts of the same anion and different cation (apart from the thiocyanates), we can see that the order is the reverse of that observed in straight thermal degradation; that is LiCl is less effective than $MgCl_2$, and KI less effective than LiI in retarding thermooxidative degradation. Our hypothesis is entirely consistent with this behavior.

As in straight thermal degradation, the anion has a marked influence on the relative oxidative stability of the complexes. In thermal oxidation the anion may play an additional role by inducing the decomposition of hydroperoxides through a nonradical route. This may be the dominating effect in the case of thiocyanate complexes where the near-identical behavior of the two salts points to the influence of the common thiocyanate anion overwhelming any differences in polarizing power of the Li^+ and K^+ cations.

We have observed that *tert*-butyl hydroperoxide is rapidly decomposed by NaSCN at room temperature and therefore propose that both thiocyanates inhibit thermooxidative degradation predominantly by decomposing hydroperoxides on the polyether; in this manner the usual chain reaction is broken.

Iodides, however, are known to reduce hydroperoxides quantitatively in the presence of acids forming iodine. We have found that the reaction occurs even in neutral medium although probably not quantitatively. Thus, we have observed that *tert*-butyl hydroperoxide reacts with LiI in ethylene glycol dimethyl ether solution at room temperature, evolving CO_2 (identified by GC-FTIR) and producing a reddish-brown solution. Therefore, iodides may exert a cumulative stabilizing influence through both cation complexation and hydroperoxide-iodide ion reaction.

Further evidence for the occurrence of these reactions comes from literature reports,[13-15] mentioned earlier, that alkali metal halides and pseudohalides accelerate the decomposition of peroxidic O-O bonds to give nonradical products (see reaction 2). In the case of thermal oxidation these processes could therefore block reaction a in Scheme I.

Additionally, if we take into account that volatilization of PEO complexes in air occurs at roughly the same temperature as straightforward thermal degradation of pure PEO (see Figures 1-3), we could also assume that the intermediate species formed by decomposition of hydroperoxides (e.g., radical III) in the presence of complexed salts undergo purely thermal degradation, even in the presence of oxygen, at lower temperatures than they do in pure PEO. In this manner, the same volatile products of thermal oxidation could be formed in both complexed and pure PEO but without leaving detectable concentrations of carbonyl species in the polymer in the former case.

Acknowledgment. A travel grant from NATO (RG 090/87) and financial support from the Minestero della Pubblica Istruzione of Italy are gratefully acknowledged. A.M.G. gratefully acknowledge financial support from the TWAS Italian Awards Scheme for Research and Training in Italian Laboratories.

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