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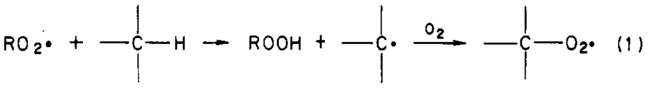
Reactivity of Polypropylene Peroxyl Radicals in the Solid State[†]

Peroxyl radicals ($RO_2\cdot$) are well established to be key intermediates in the oxidation of alkyl groups (R·) in the liquid phase.[1] Each radical is consumed largely by atack on a labile C–H group to generate a hydroperoxide and an alkyl radical which rapidly combines with dissovled oxygen to re-form the peroxyl radical (reaction 1). Although these



$$RO_2\cdot + -\overset{|}{\underset{|}{C}}-H \rightarrow ROOH + -\overset{|}{\underset{|}{C}}\cdot \xrightarrow{O_2} -\overset{|}{\underset{|}{C}}-O_2\cdot \quad (1)$$

steps have been confirmed in the liquid phase, their role in the oxidative deterioration of polymers is based on indirect evidence, such as the analysis of the final oxidation products. Attempts at the direct observations of these steps have led to conflicting results. For example, the formation and decay of peroxyl radicals ($PPO_2\cdot$) in solid polypropylene (PPH) have been extensively studied.[2-10] Radicals have usually been generated by irradiation (UV on preoxidized polymer, electron beam, and X- or γ-irradiation of virgin polymer). However, quite diverse conclusions have been reached concerning the interpretation of the electron spin resonance (ESR) spectra of these radicals and their reactivity. From the line shape and decay kinetics, they have been variously claimed to be entirely in the amorphous domains[5,9] or entirely in the crystalline domains,[7] in both domains with differing mobility,[4] or in only one domain but with restricted rotational movement.[8] Several attempts have been made to observe the macroperoxyl propagation step (reaction 2a) by looking

$$PPO_2\cdot + PP\text{-}H \rightarrow PPOOH + PP\cdot \qquad (2a)$$

$$PP\cdot \xrightarrow{O_2} PPO_2\cdot \qquad (2b)$$

for the formation of macroalkyl (PP·) radicals when a peroxyl population was held under vacuum. Some studies detected no propagation,[2,4] while others observed macroalkyl formation.[3,4,6,7] Recently, Reuben and Mahlman suggested an alternative way of directly observing reaction 2.[10] By electron beam irradiation of PPH in an $^{17}O_2$ atmosphere, ^{17}O-labeled peroxyl radicals were generated and their reaction was then followed at room temperature, but in an $^{16}O_2$ atmosphere. The distinctive changes in the ESR spectra which indicated $PP^{17}O_2\cdot$ to $PP^{16}O_2\cdot$ conversion (by reactions 2a and 2b) were expected. However, no conversion was observed despite protracted reaction times and only the steady loss of the overall $PP^{17}O_2\cdot$ population was seen.

These diverse observations lead to the question of who is correct—anyone or everyone? The ^{17}O study led Reuben and Mahlman to the inescapable conclusion that their macroperoxyl radicals did not propagate; yet this contradicts classical hydrocarbon oxidation theory, which has previously been found to explain the solid-state oxidation of polymers reasonably well.[11] As part of the comprehensive study of the reactivity of macroperoxyl radicals in oxidizing PPH, we have attempted to resolve these problems by repeating studies of macroperoxyl to macroalkyl transformation and of $PP^{17}O_2\cdot$ to $PP^{16}O_2\cdot$ conversion for radicals of carefully controlled history.

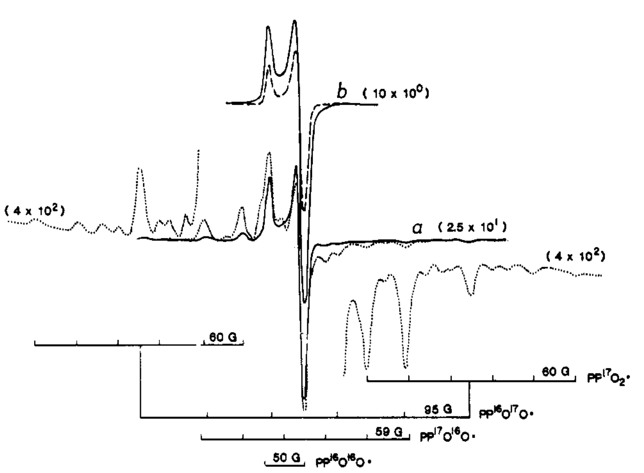


Figure 1. Macroperoxyl ESR spectra at 77 K (10 mW). Amplifier gain values are shown in parentheses. a: (- - -) After 2-Mrad γ-exposure at –77 °C in $^{17}O/^{18}O/^{16}O$ atmosphere (stored continuously at low temperature); (—) as for above, but warmed to 23 °C for 15 min and saturated with $^{16}O_2$. b: (—) New film sample, as for (a), but irradiated in $^{16}O_2$ and maintained continuously at low temperature; (- - -) as for above, but warmed to 23 °C for 15 min and saturated with $^{16}O_2$.

Spectra were recorded on a Varian E4 ESR spectrometer using a microwave power of 10 mW for peroxyl signals alone and 1.0 mW for any signal containing macroalkyls. These power values gave negligible signal saturation for $PPO_2\cdot$ and PP· with our spectrometer. Where possible, radical concentrations were derived by electronic double integration (Nicolet 1170) relative to both a ruby resident in the cavity and by substitution with a benzene solution of DPPH. Although a range of PPH morphologies was studied, results are presented here only for commercial film (Hercules resin, 30 μm) and as polymerized powder similar to that studied previously.[10] Film and powder samples were γ-irradiated in an Atomic Energy of Canada Gammacell 200 (1.35 Mrad h^{-1}). All samples were exposed in glass equipment and transferred (at 77 K when necessary) to fresh ESR tubes to avoid the complication of trapped spins in the glassware. Polymer samples were irradiated and aged in air, normal oxygen ($^{16}O_2$), or an ^{17}O atmosphere (60 atom % ^{17}O, 23 atom % ^{18}O, balance ^{16}O, highest enrichment commercially available, MSD Isotope).

The γ-irradiation of PPH film in the ^{17}O atmoshere at –78 °C gave the expected composite ESR spectrum from the macroradicals $PP^{16}O_2\cdot$, $PP^{17}O_2\cdot$, $PP^{17}O^{16}O\cdot$, and $PP^{16}O^{17}O\cdot$ (Figure 1). For simplicity, ^{18}O radicals are not listed as they have ESR spectra identical with those of ^{16}O species (both have nuclear spin of zero). The $^5/_2$ spin of the ^{17}O nucleus causes the overlayed sixfold splittings shown in Figure 1. Our derived stick diagram and hyperfine splittings shown in Figure 1 are quite similar to those reported for ^{17}O-labeled peroxyl radicals from poly(tetrafluoroethylene).[12] For clarity, only the outermost $PP^{17}O_2\cdot$ lines are indicated in the stick diagram. At –78 °C, we have confirmed that $PPO_2\cdot$ radicals are indefinitely stable, so that $PPO_2\cdot$ radicals observed after γ-exposure at –78 °C neither propagate nor terminate but accumulate, possibly in clusters of 2 or 3 radical pairs close to each site of γ-ray photon/polymer interaction.[13] This population can be preserved at –78 °C while the ^{17}O atmosphere is removed (≥5 h at high vacuum) and ^{16}O is introduced and allowed to diffuse throughout the PPH film sample (normally 15 h allowed).

Upon warming to 23 °C, in $^{16}O_2$, the labeled $PPO_2\cdot$ population initially both decayed rapidly in integrated intensity and showed a rapid change in ESR hyperfine structure. After a brief time at 23 °C, all reactions were stopped by cooling to 77 K and an ESR spectrum was recorded under conitions identical with those used prior to the decay (Figure 1). Clearly the ^{17}O hyperfine structure is extensively reduced and the new line shape resembles that of the $PP^{16}O_2\cdot$ line shape at 77 K, obtained when the

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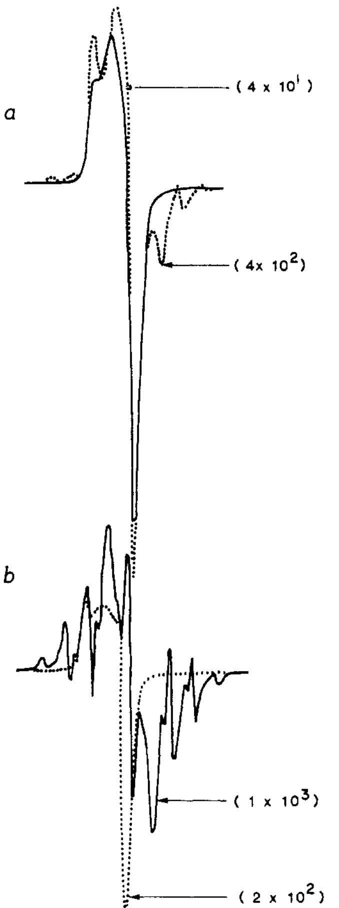

Figure 2. Macroradical ESR spectra at 23 °C (1.0 mW). Amplifier gain values are shown in parentheses. a: (—) After 5-Mrad γ-exposure at −77 °C in $^{16}O_2$ atmosphere (immediately after warming to 23 °C (~2 min under vacuum); (- - -) as for above, but stored at 23 °C under vacuum for 4 h. b: (—) New film sample, as for (a), but irradiated under vacuum and stored under vacuum at 23 °C for 3 h; (- - -) as for (a) but stored at 23 °C under O_2 for 4 h.

polymer is γ-irradiated at −78 °C in $^{16}O_2$ and allowed to decay for a similar time at 23 °C (shown in Figure 1b for comparison). These changes are consistent with the occurrence of reactions 2a and 2b together with radical–radical annihilation.

In a separate series of experiments, when a conventional peroxyl ($PP^{16}O_2\cdot$) population was generated by γ-irradiation at −78 °C in $^{16}O_2$, decay of these radicals after complete removal of all O_2 under high vacuum at −78 °C led to the changes shown in Figure 2. The new spectral features are consistent with partial conversion to macroalkyl radicals (shown for comparison in Figure 2) expected from reaction 2a. The macroalkyl yield was ~20% of the initial $PPO_2\cdot$ level, most $PPO_2\cdot$ terminating. Also shown in Figure 2 is the line shape after $PPO_2\cdot$ decay in air. Admission of O_2 resulted in the complete loss of alkyl and re-formation of $PPO_2\cdot$ within about 30 s.

Further experiments showed that radical history had a dramtic effect on peroxyl reactivity. For example, when a radical population was allowed to decay naturally (in the ^{17}O atmosphere for $PP^{17}O_2\cdot$ or normal air for $PP^{16}O_2\cdot$) at 23 °C for 7 h or longer, very little $PP^{17}O_2\cdot$ to $PP^{16}O_2\cdot$ conversion was observed upon conversion to a $^{16}O_2$ atmosphere (Figure 3) and very little PP· formation was seen when the $PP^{16}O_2\cdot$ population was placed under vacuum (not shown). In both cases, the fate of the peroxyl radicals was apparently simply to decay without forming new, detectable free-radical species, essentially as observed by several researchers.[2,4,10] Of particular significance is the fact that some of the initially ^{17}O-labeled radicals were still detectable after extended periods in normal air at room temperature, despite these radicals having originated during the initial γ-exposure. In fact the $[PP^{17}O_2\cdot]/[PP^{16}O_2\cdot]$ concentration ratio in the dying population actually increased slowly at long reaction times, implying that a portion of the first-generated radicals are particularly unreactive. The 23 °C, ^{17}O-labeled peroxyl spectrum that we observed after 7 h in the ^{17}O atmosphere at 23 °C (Figure 3) is identical with that reported by Reuben and Mahlman, as is the low conversion to $PP^{16}O_2$ of this population.[10]

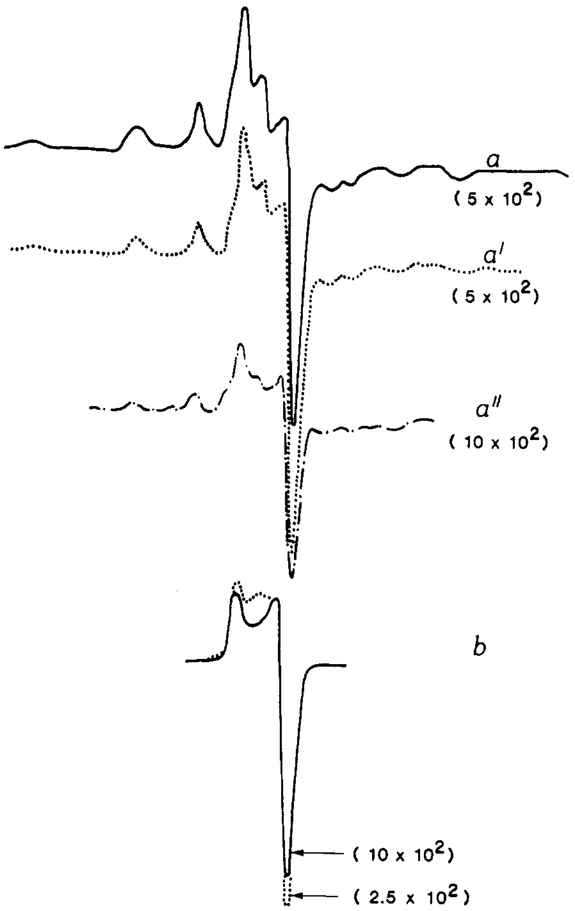

Figure 3. Long-lived macroperoxyl radical spectra at 23 °C (10 mW). Amplifier gain values are shown in parentheses. a: After 2-Mrad γ-exposure at −77 °C in $^{17}O/^{18}O/^{16}O$ atmosphere (stored for 7 h under this atmosphere at 23 °C). a′: Sample a after atmosphere is changed to $^{16}O_2$ and 3.75 h at 23 °C under $^{16}O_2$. a″: Sample a′ after 140 h under $^{16}O_2$ at 23 °C. b: (- - -) New film sample, after 2-Mrad exposure at −77 °C in $^{16}O_2$, (stored 7 h under $^{16}O_2$ at 23 °C); (—) as for above, but stored 140 h at 23 °C under $^{16}O_2$.

The dramatic difference in reactivity between the initial and "aged" macroperoxyl populations can be rationalized in terms of radical mobility. We have found that propagation and termination rates of macroperoxyl radicals in PPH are extremely sensitive to the mobility of their immediate environment.[14] This was shown by a ~20-fold decrease in apparent termination rate constant on going from almost completely amorphous, atactic polypropylene to semicrystalline isotatic samples or more morphologically perfect samples such as the as-polymeized powder, similar to that used by Reuben and Mahlman.[10] The use of temperature to control $PPO_2\cdot$ reactivity is well established.

Radical mobility in the polymer can be expected to be controlled by chemical cross-linking (for example, peroxide bridges between chain segments) as well as the morphological perfection of its environment. Roginskii et al. have shown that peroxyl radical reactivity drops with increased levels of polymer oxidation.[5] We suggest that in the initial macroperoxyl population, a fraction of the radicals behave as if they are in motionally restricted domains and are unable to propagate. They can however terminate when another radical passes close by, moving by a combination of physical site transport (e.g., segmental oscillation, reptation etc.) and reactive migration (sequences of reactions 2a and 2b). The change in ESR line shape of $PP^{16}O_2\cdot$ at room temperature as the popultion "ages" is consistent with the concept of mobile and trapped radicals. For example, after protracted decay time at 23 °C, the ESR line shape is a sharp anisotropic singlet (Figure 1) identical with all $PP^{16}O_2\cdot$ spectra at 77 K, when there is negligible mobility.[15] The concept of peroxyl radicals trapped in "crystalline" domains has frequently been invoked.[4,7] However, it must be emphasized that only peroxyl radical signals are detected immediately after γ-irradiation of semicrystalline PPH in air or within 2 min after admitting O_2 to a PPH sample irradiated under vacuum. This means that all macroalkyls (the precursors of the peroxyl radicals) generated by γ-irradiation are O_2 accessible, either because "crystalline" domains in normal PPH samples (i.e., not exhaustively annealed) are highly defective and so O_2 permeable or because macroalkyl sites migrate rapidly into the amorphous regions by a hydrogen-transfer process.

The failure of $PP^{17}O_2\cdot$ radicals to propagate in the Reuben and Mahlman study probably stems from the nature of their sample (as-polymerized PPH powder gave much slower rates of radical decay than melt-quenched film in air experiments) and the history of their radicals.[10] Unfortunately, little precise information on irradiation conditions and postirradiation conditions was given in their paper, but it is reasonable to expect some sample heating during their 10-s electron beam exposure, which would cause a dramatic drop in radical population before the sample reached the ESR spectrometer "shortly after irradiation". Consequently, only the relatively immobile and unreactive ("aged") fraction of the population would be detected.

Although the formation of macroalkyl radicals from peroxyl radicals and the $PP^{17}O_2\cdot$ to $PP^{16}O_2\cdot$ conversion are consistent with the classical oxidative propagation step (reaction 2a), both effects could result from the complex interaction of *tert*-peroxyl radicals, the fate of over 60% the initial peroxyl population.[11] In an attempt to resolve this problem, we are currently combining ESR and Fourier transform infrared spectroscopy to examine the products generated during the decay of a $PPO_2\cdot$ population.

In summary our overall conclusions are that macroperoxyl radical reactivity is controlled by mobility factors, so that the radicals may be highly reactive to propagation or termination or extremely unreactive. The proportions of each type of radical present will depend markedly on the precise morphology of the sample, irradiation conditions, and subsequent thermal history of the radical ("aged") population. All of the diverse $PPO_2\cdot$ behavior reported in the literature can be reproduced by the correct combination of the above factors. Both the highly reactive "mobile" $PPO_2\cdot$ and the less reactive "trapped" radicals appear to contribute to the degradation of the polymer. However, we believe that the thermal decomposition of the macrohydroperoxide groups becomes the dominant initiation mechanism for the prolonged oxidation which develops subsequent to γ-irradiation.[16]

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Conformational Analysis of Poly(di-*n*-hexylsilylene)

Polysilane polymers are a scientifically interesting class of materials for which numerous applications have been described.[1] Of special interest is the remarkable ultraviolet (UV) absorption spectra exhibited by these polymers.[2] Alkyl-substituted polysilanes absorb strongly in the mid-UV, with λ_{max} typically residing within the 305-326-nm range.[1-4] The location of this absorption maxima at room temperature ($\lambda_{max,RT}$) shows an interesting correlation with the relative steric bulk of the alkyl substituent. The observed UV $\lambda_{max,RT}$ occurs at longer wavelengths when the alkyl substituents are more sterically demanding. A recent addition to this list of interesting spectral properties is the observation that polysilane polymers are thermochromic both in solution and in thin films.[5] Bathochromic shifts for UV λ_{max} upon cooling are found to be as large as 44 nm in solution and 55 nm in films. The present study was undertaken in order to explore possible relationships between the ground-state molecular structure of polysilane polymers and their observed thermochromic behavior.

Bonding in polysilanes has been described previously in terms of a linear combination of atomic orbitals (LCAO) model.[6] This model predicts that the HOMO-LUMO energy separation for a polysilane chain will be smaller in the trans conformation than in the gauche. Based on this it has been suggested[5] that the thermochromic behavior exhibited by polysilane polymers is the result of a temperature-dependent conformational change along the polymer backbone. As the temperature decreases, the population of the trans conformation increases, resulting in the observed bathochromic shift in UV λ_{max}. Implicit in this interpretation is that the ground-state conformation for these polysilane polymers is trans. Unfortunately,