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Polypropylene Oxidation: The Apparent Rate Constant for Peroxy Radical Termination and the Photoinitiation Efficiency[‡]

A. Garton,* D. J. Carlsson, and D. M. Wiles

Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR9.

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ABSTRACT: The decay of peroxy radicals in a series of photooxidizing polypropylene films upon cessation of irradiation has been examined, using electron spin resonance spectroscopy. Rate constants for peroxy radical termination of 1–8 $M^{-1}\,s^{-1}$ have been observed. The efficiency of the initiation process has been found to be $\sim 10^{-3}$ by using these data and a knowledge of the rate of radical generation during irradiation. The significance of these very low termination constants and initiation efficiencies is discussed in terms of the low mobility of polymeric peroxy radicals in a polymer matrix.

There is considerable interest in the values of the rate constants associated with the autoxidation of solid polypropylene (PPH).[1-7] A recent critical review by Mayo[1] has rationalized much of the published literature on the rate constants k_p and $2k_t$ for the propagation and termination of polymeric tertiary peroxy radicals ($PPO_2\cdot$) (reactions 1 and 2). However, the work reviewed depends upon the use of appreciable concentrations of thermal initiators (with their associated compatibility and plasticization problems) and/or free-radical scavengers which may not give a valid estimation of the important propagating radicals.[8] We report here some observations concerning the decay in peroxy radical concentration that occurs in a photooxidizing PPH film sample upon cessation of irradiation, essentially as described by Roginskii et al.[3,5] The rate of decay gives $2k_t$ directly, and when this is combined with a knowledge of the radical concentration and the rate of radical generation during irradiation it also gives the efficiency of macroperoxy radical production during the initiation step. The advantage of this method of determining kinetic parameters is that as well as being experimentally simple and direct it also allows rate constants to be determined under near normal photooxidation conditions without the use of additional initiators or radical scavengers.

$$PPO_2\cdot + PPH \xrightarrow{k_p} PPOOH + PP\cdot \qquad (1)$$

$$PPO_2\cdot + PPO_2\cdot \xrightarrow{2k_t} \text{nonradical products} \qquad (2)$$

Isotactic polypropylene film (Enjay, chill-roll cast, 25 μm thick, Soxhlet extracted with acetone and vacuum dried) was irradiated in a xenon arc Weather-Ometer.[9] Samples ($\sim$100 mg) were removed at chosen irradiation times and inserted, tightly rolled, into electron spin resonance (ESR) tubes. In this way ESR spectra could be obtained from uniformly irradiated film samples within 5 min of the end of irradiation. Radical concentrations were estimated by double integration of the ESR signals and comparison with a standard (4-oxo-2,2,6,6-tetramethylpiperidine-*N*-oxyl). A typical ESR spectrum is shown in Figure 1 and corresponds well to that of a peroxy radical in a polymer matrix.[3,6,7] The decay of the ESR signal was then followed for several hours at 25 °C in the cavity of the spectrometer. Hydroperoxide concentrations were measured by infrared spectroscopy.[9]

From a comparison of the spectral intensity distribution of the output of the Weather-Ometer under our operating conditions with the absorption spectrum of the hydroperoxide chromophore, we have previously determined that the rate of radical production by hydroperoxide photolysis (the dominant photoinitiation process[10]) is given by eq 3.

$$PPOOH \xrightarrow{h\nu} PPO\cdot + \cdot OH \xrightarrow{PPH/O_2} 2PPO_2\cdot \qquad (3a)$$

$$d[PPO_2\cdot]/dt = 0.6 \times 10^{-5} f[PPOOH] \qquad (3b)$$

[PPOOH] is the molar hydroperoxide concentration and f is the efficiency of generating propagating peroxy radicals from the hydroperoxide cleavage. For 50% crystalline isotactic PPH, only the amorphous phase is assumed to oxidize so that all concentrations quoted are twice those determined experimentally for the film as a whole. A primary quantum yield of 2 for radical production from

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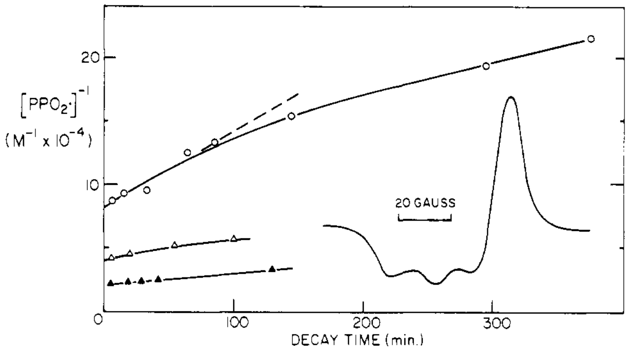

Figure 1. Decay of macroperoxy radicals in polypropylene. Isotactic film, photooxidized to 0.12 M PPOOH in a xenon arc Weather-Ometer (~60 h): (○) decay immediately on cessation of UV exposure; and (▲) decay immediately after γ irradiation (90 min at 8000 rad min^{-1} in air). Atactic powder, γ irradiation only: (△) decay immediately after γ irradiation (30 min at 8000 rad min^{-1} in air). The typical radical signal shown has $g_{av} = 2.018$.

the hydroperoxide photolysis step is assumed.[9] For reaction 2, the rate of peroxy radical recombination is given by eq 4. When irradiation is interrupted, a plot of $[PPO_2\cdot]^{-1}$ vs. time will have a slope of $2k_t$ (i.e., the apparent rate constant for termination). From the plot shown in Figure 1, it should be noted that $2k_t$ is very low (8 M^{-1} s^{-1}) and that the second-order plot shows appreciable curvature. This curvature may result, for example, from some nonuniformity in the $PPO_2\cdot$ concentration or variations in $2k_t$ caused by its dependence on a diffusive process.[11]

$$-d[PPO_2\cdot]/dt = 2k_t[PPO_2\cdot]^2 \qquad (4)$$

Also shown in Figure 1 is the decay of peroxy radicals produced by brief γ irradiation of a film sample identical with the one described above (i.e., 0.12 M -OOH). The decay of peroxy radicals produced by γ irradiation is much slower ($2k_t \sim 1$ M^{-1} s^{-1}) than those produced by photooxidation. To confirm that the radicals being observed were not, for example, simply those trapped in or around crystalline domains[2] in the isotactic polymer, an atactic polypropylene (Montecatini, reprecipitated from toluene, irradiated as a finely ground powder) was also γ irradiated. In this low molecular weight noncrystalline polymer the decay of radicals was also slow ($2k_t \sim 3$ M^{-1} s^{-1}).

If initial radical concentrations are calculated by back extrapolation of the plots in Figure 1, initiation efficiencies (f) may be calculated by combining eq 3 and 4 and using the PPOOH concentration. In such a way it was concluded that the efficiency of initiation was very low. For example, $f = 1.4 \times 10^{-3}$ for the photooxidizing film shown in Figure 1. To confirm that back extrapolation of the radical concentration data in Figure 1 to zero time was valid, several film samples were irradiated in the ESR cavity. For example, a film sample, which had previously been irradiated in the Weather-Ometer to produce 0.08 M hydroperoxide, was wound around the inside of an ESR tube. The tube was then rotated at 10 rpm in the ESR cavity while being exposed to radiation from a medium-pressure mercury lamp (water infrared and Corning 0-53 UV filters, $\lambda > 280$ nm). On interrupting the irradiation, the decay of the double integral of the ESR signal could then be followed from an accurately determined zero-time value, after irradiation under conditions which approximate to those experienced in the Weather-Ometer. These $[PPO_2\cdot]$ decay data measured from zero time confirmed the validity of the back extrapolation of the longer-time data (>5 min in Figure 1) to the zero-time value.

The major outcome of this preliminary work is a better understanding of the very low efficiency of initiation of polypropylene photooxidation at ambient temperatures. Our value of $f \sim 1 \times 10^{-3}$ is appreciably lower than, for example, the value of 0.043 reported[4] for the efficiency of radical production on the thermal decomposition of polypropylene hydroperoxide at 65 °C or the value of ~0.01 calculated for the efficiency of producing propagating peroxy radicals from the thermal decomposition of di-*tert*-butyl peroxyoxylate in atactic polypropylene at 45 °C.[7]

We attribute this difference largely to the different methods by which f was determined. The use of a radical scavenger[1,2,4,7] at a sufficiently high concentration[12] will give a measure of the number of radicals which escape the primary initiation cage (i.e., the immediate vicinity of the initiation event). To assume that the radicals which escape primary cage recombination then become uniformly distributed in the polymer and terminate statistically ignores the very low mobility available to polymeric radicals in a polymer matrix. Even after several propagation steps, a peroxy radical pair from the same primary cage will still be sufficiently close that their recombination has a relatively high probability. This is analogous to the concept of secondary cage recombination discussed in depth by Noyes[12] and by Walling and Lepley.[13] We have discussed elsewhere[8] the theoretical background and consequences of secondary cage recombination in solid polymers. The consequence most relevant to the present discussion is that a large proportion of peroxy radical pairs will recombine after only a few propagation steps and so contribute little to the instantaneous radical population. Those radicals which escape secondary cage recombination will have very long lifetimes before terminating with peroxy radicals from other initiation events. It should be noted that even though only a few radicals escape secondary cage recombination, their contribution to the instantaneous radical population after prolonged irradiation will be heavily weighted because of their long lifetimes. A kinetically determined f, as reported here, will therefore approximate to a measure of the efficiency of producing radicals which escape both primary *and* secondary cage recombination processes. However, the use of a radical scavenger[1,2,4,6] should count most peroxy radicals which propagate from the primary cage because the secondary cage will be (at least in part) accessible to the radical scavenger.[12]

Our values of $2k_t$ (1–8 M^{-1} s^{-1} at 25 °C) are lower than that suggested by Mayo[1,7] (~25 M^{-1} s^{-1}, extrapolated) and those reported by Roginskii et al.[3,5] (6–170 M^{-1} s^{-1}, depending upon [PPOOH]). However, consideration of the mechanistic significance of $2k_t$ lends support to Buchachenko's[14] conclusion that the value of $2k_t$ can have little firm meaning. For example the experimentally observed value of $2k_t$ must be very dependent on the history of the radical population and the precise nature of the sample. The observed $2k_t$ will be a composite factor encompassing many types of peroxy radicals (largely tertiary, but with some primary,[1] also those at chain ends or on low molecular weight fractions, etc.). Furthermore, radical pairs observed very soon after their production will terminate very quickly[5,8] because of the small separation of the radical pairs and so raise the apparent overall $2k_t$ value which is calculated assuming a random distribution of peroxy radicals. After prolonged UV irradiation, the long-lived radicals represent a large fraction of the radical population, and their apparent $2k_t$ will be lower (~8 M^{-1} s^{-1}) because the radicals will, on average, be more widely separated. In addition, localization of the oxidation will also result in a high probability of the primary and secondary oxidation products influencing the oxidation process. After γ irradiation, $2k_t$ is even lower (1–3 M^{-1} s^{-1}) possibly because

γ oxidation is initiated indiscriminately, largely at random through the polymer matrix, whereas photooxidation, at least at ambient temperatures, must lead to the production of highly localized zones of high oxidation-product concentration.[14]

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The Kinetics of Triplet Processes in Poly(*N*-vinylcarbazole) from 77 to 298 K

R. D. Burkhart* and R. G. Avilés

Department of Chemistry, University of Nevada, Reno, Nevada 89557.

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ABSTRACT: The delayed fluorescence intensity, I_{DF}, from solid films of poly(*N*-vinylcarbazole) has a temperature dependence which includes two extrema, a minimum at about 145 K and a maximum at about 200 K. Using a trapping–detrapping model originally worked out by Siebrand for an arbitrary number of traps, we can satisfactorily interpret the present data in terms of two traps. A calculated depth for the deep trap agrees to within 20% of the experimentally derived value. The delayed fluorescence decay times are multiexponential over the temperature range studied, but a fast component having a lifetime between 2.0 and 3.6 ms between 77 and 140 K was isolated and was attributed to triplet–triplet annihilation involving directly formed mobile triplets. Similar experiments at room temperature indicate that the mobile triplet lifetime has very little temperature dependence and an average value of about 7 ms. Longer lived delayed fluorescence lifetimes in the low-temperature region arise from interactions between trapped triplets and indirectly formed mobile triplets produced from detrapping.

Poly(*N*-vinylcarbazole) (PVCA) is a photophysically active substance which emits prompt fluorescence, delayed fluorescence (DF) and phosphorescence. It is also photoconductive.[1] The fluorescence spectrum is of the excimer type with two emitting components at 420 and 375 nm.[2] Both spectral and kinetic data[3,4] have also been obtained indicating two excimer-like components in the phosphorescence of PVCA solid films. The temperature dependence of the fluorescence intensity of PVCA solutions was reported by Johnson,[5] and a study of the temperature dependence of the phosphorescence of PVCA solid films has recently been completed in these laboratories.[4]

In both the singlet and the triplet manifolds, it appears that migrating excitons are trapped at various sites in the polymer structure. Time-resolved fluorescence spectra[6,7] indicate that the shallow traps which lead to 375-nm emission are preformed sites. It is not clear whether or not the deep trap sites are preformed, but it does seem that an interconversion of shallow excimer to deep excimer can occur. It has been suggested that the shallow species corresponds to a partial overlapping of the carbazolyl aromatic rings and that the deep one involves a sandwich-like arrangement of carbazolyl groups.

From studies of the temperature dependence of the phosphorescence lifetimes, triplet trap depths of 0.6 and 3.0 kcal/mol have been determined.[4] Above about 90 K, the emission from shallow traps is very feeble, and from 145 K to room temperature the phosphorescence decays are best characterized by a single exponential. At ambient temperatures, the deep trap phosphorescence has all but disappeared and can only be detected from carefully purified samples.

The role of mobile triplet excitons in these delayed luminescence processes has received relatively little attention. Itaya and co-workers[9] found that phosphorescence lifetimes were unaffected by the incorporation of naphthalene as a triplet quencher but that intensities were markedly reduced. This not only lends further support to the belief that phosphorescence emission originates from immobilized species but also makes possible a Stern–Volmer treatment leading to a quencher rate constant, the value of which is thought to be determined by the rate of mobile exciton hopping. Perhaps it should be emphasized that in this rigid system the term "mobility" carries with it the implication of chromophore-to-chromophore energy transfer, not bulk translational motion.

In their analysis of the Stern–Volmer experiments, Itaya et al. assumed that the mobile triplet lifetime was twice the delayed fluorescence lifetime at 77 K; however, it is not clear that the factor-of-two relation holds for these films since it has not been conclusively shown that delayed fluorescence results exclusively from the homofusion of two mobile triplets. Klöpffer and Bauser[2] have suggested that mobile triplet–trapped triplet interactions may be the source of delayed fluorescence, and since a significant population of trapped triplets exists at 77 K, this would appear to be a very reasonable suggestion. Furthermore, DF lifetimes at 77K show a definite multiexponentiality as will be demonstrated below. Earlier work on the temperature dependence of PVCA delayed fluorescence[10] has

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