JOURNAL OF CATALYSIS 31, 372–376 (1973)

Tetralin Oxidation in the Presence of Polymers: Evidence of Initiation by Surface Free Radicals

P. S. MODY, N. D. ORLANDO, J. M. SCHULTZ, AND B. C. GATES

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19711

Received May 29, 1973

Oxidation of Tetralin at 50 to 88°C in the presence of particles of polyethylene (or polypropylene) was characterized by rates of oxygen uptake in a standard autoxidation apparatus. The induction time for reaction was reduced either by grinding or by γ-irradiation of the polymer particles. The results suggest a sequence of autoxidation reaction steps initiated by polymer surface free radicals, which can be formed by irradiation or by scission of C–C bonds in the tie chains connecting the chain-folded lamellae of linear polyethylene.

INTRODUCTION

An unexpected catalytic activity of polyethylene, polypropylene, and polytetrafluoroethylene for oxidation of Tetralin has been demonstrated by Taylor (*1*, *2*), who observed rates of reaction per unit surface area which were roughly equal to those found for a number of metal oxide catalysts (*3*). Product distributions established Tetralin hydroperoxide as a primary product of the oxidation, and identities of the other products demonstrated that the reactions involved free radical intermediates, which also occur in the homogeneous Tetralin oxidation initiated by free radicals. Taylor's results raise an interesting question: What are the surface sites, perhaps common to these polymers, that cause acceleration of the Tetralin oxidation? The Tetralin oxidation kinetics and ESR data reported here provide a preliminary answer, indicating the role of surface free radicals.

NOMENCLATURE

C	concentration in reaction mixture
$\mathbf{k}$	second-order rate constant
RH	Tetralin
$R_p^{\cdot}$	polymer surface free radical
$\mathbf{r}$	steady-state rate of Tetralin oxidation
W	mass of polymer in reaction mixture

EXPERIMENTAL METHODS

Rates of Tetralin oxidation were determined from measured rates of oxygen consumption in a standard, constant-pressure autoxidation apparatus (*4*). In a typical experiment, 0.3 g of polymer particles were suspended in 4 ml of reactant solution (50 vol % Tetralin in chlorobenzene) in a 25 ml sidearm Pyrex flask with ports for an immersion thermometer and for sample withdrawal through a rubber syringe cap. The reactor was immersed in a constant-temperature bath controlled to ±0.5°C, and the contents were stirred with a glass-covered magnetic stirring rod. Tetralin was degassed before experiments by repeated cycles of freezing with liquid N_2, evacuation, and thawing. Oxygen uptake during reaction was monitored for reaction at 1 atm and temperatures between 50 and 88°C. Details of the procedure, which was nearly identical to Taylor's, are given by Mody (*5*).

Fisher purified Tetralin was used; gas chromatographic analysis showed that the reagent was purer than the practical grade reagent purified by sulfuric acid extraction according to Taylor's method (*1*). The Tetralin was diluted with laboratory grade chlorobenzene (Matheson, Coleman, and Bell).

The polymers were Phillips Marlex 6009 linear polyethylene and Shell 5120S isotactic polypropylene. The 60 to 80 mesh powders were obtained by screening ground samples. Grinding was done in a Waring blender cooled with liquid N_2.

ESR spectra of polymers ground and measured in air were obtained with a Varian V-4502 spectrometer having an X-band ($\nu \approx 9.5$ GHz) microwave bridge and a time-averaging computer. Samples were held in 4-mm quartz tubes.

RESULTS AND DISCUSSION

Data for oxygen uptake during reaction of Tetralin are similar to those of Taylor; the results of Fig. 1 are typical, showing an induction period followed by a period of nearly constant rate. In the following section we refer to the slope of the line through the points as the steady-state rate and to the abscissa intercept as the induction period. Since results were not significantly dependent on the stirrer speed, we infer that the kinetics of oxidation were not significantly affected by the mass transport of oxygen through the reactant solution.

Results for a series of variously prepared polyethylenes gave results which were indistinguishable within experimental error. The polymers were a solution-crystallized specimen, an as-melt-crystallized polyethylene, and a melt-crystallized material etched with red fuming nitric acid. Idealized depictions of the microstructures of the three preparations are shown in Fig. 2. The differences are the following: The solution-crystallized specimen was expected to exhibit a greater area of fold surface than the melt-crystallized products, with the folds better defined (*6*); the acid-etched specimen was expected to have surface $-NO_2$ and $-OOH$ groups (*7*), and should also have exhibited greater permeability to reactants, since interlamellar material was leached out (*8*). Since all three polyethylenes showed the same catalytic behavior, and since Taylor found polyethylene to be catalytically similar to polypropylene and polytetrafluoroethylene, we conclude that the catalytic sites depend neither on surface topography nor on the presence of functional groups formed in oxidation.

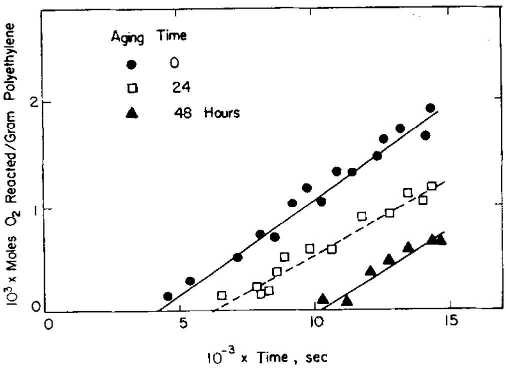

FIG. 1. Effect of aging of ground polyethylene on the uptake of oxygen during Tetralin oxidation at 65°C.

The data of Fig. 1 show, however, that the Tetralin oxidation was significantly affected by the time during which ground polyethylene was aged in air at room temperature prior to reaction. Similar results were observed for polyethylene and polypropylene at other temperatures (*5*). In general the induction times increased as the aging time increased. At all temperatures the effect was more pronounced with polyethylene than with polypropylene. For both polymers the influence of aging time decreased with increasing reaction temperature, and the curves at 0 and 48 hr for polypropylene at 88°C were indistinguishable. Aging of the ground polymers had no significant effect on the steady-state oxidation rate.

Since this set of results implies that the induction time was reduced by grinding of the polymers, and since ESR experiments have shown that grinding produces allyl and alkyl radical groups where C–C bonds are broken during formation of polymer surfaces (*9*), we postulate that mechanically induced surface free radicals were

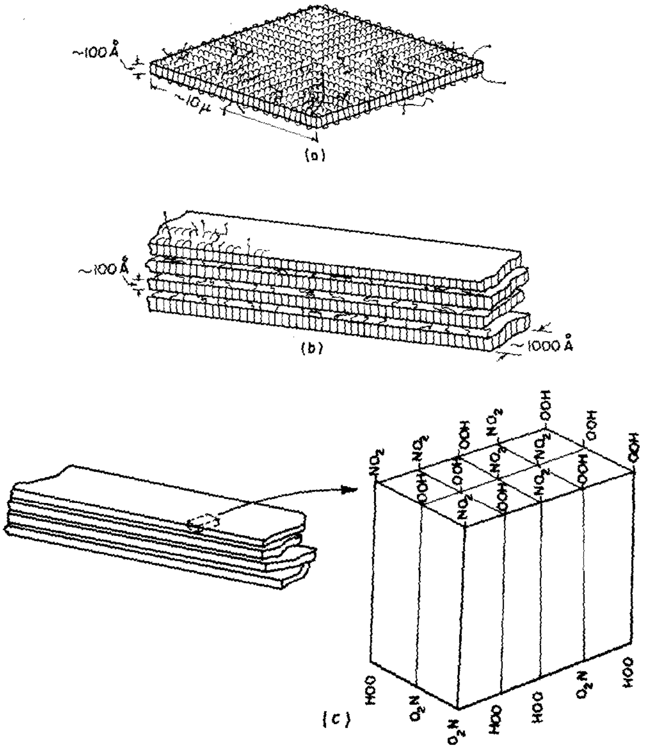

FIG. 2. Models of polyethylene preparations: (a) single crystals; note the large chain-folded surface exposed; (b) melt-crystallized material; note the greater relative exposure of lateral surface; (c) HNO_3-etched material; note the -OOH and -NO_2 groups attached to the basal surfaces.

responsible for initiation of the oxidation reaction; these radicals might have been oxidized species, perhaps relatively stable peroxy radicals (*9*).

Corresponding to this postulate, the induction period was only weakly dependent on temperature. The apparent activation energy (estimated from a semilogarithmic plot of inverse induction period versus inverse temperature) was about 5 kcal/mole for polyethylene and about 2 kcal/mole for polypropylene. In contrast, Taylor reported a value of 17 kcal/mole for polytetrafluoroethylene.

Two experiments were attempted to test the hypothesis that the Tetralin oxidation was initiated by surface free radicals. The first involved creation of surface free radicals by γ-irradiation and observation of the influence on the induction period of radical concentration, as measured by ESR. The second involved seeking a relation between induction period and the decay of surface free radicals during aging of unirradiated ground particles.

Free radicals were produced in polyethylene, presumably throughout the bulk of the material (*10*), by ^{60}Co irradiation of particles ground at liquid N_2 temperature. As expected, a correlation between free radical concentration (spin concentration) and radiation dose was found (Table 1). Immediately after irradiation, particles were charged to the autoxidation reactor. Figure 3 shows the effect of radiation dose on the oxygen uptake in the presence of

TABLE 1
DEPENDENCE OF SPIN CONCENTRATION IN POLYETHYLENE ON RADIATION DOSE

Dose (Mrad)	$10^{14} \times$ Spins/cm^3
0.0464	3.1
0.1856	5.4
0.3712	9.3

polyethylene at 65°C. The induction time decreased and the steady-state rate increased with increased irradiation. Results at the other reaction temperatures were qualitatively the same. These results confirm the hypothesis that the reaction was initiated by surface free radicals.

ESR studies of unirradiated, freshly ground polymers yielded no signal. Since spectra showed that spin concentrations less that about 10^{14} cm^{-3} were undetectable with this instrument, we infer that surface free radicals in unirradiated polyethylene were present in concentrations less than about 10^{14} cm^{-3}.

This result is consistent with the model proposed. If all the chains intersecting the fracture surface were broken, the radical concentration (number of broken bonds per cubic centimeter of polymer) would be about 10^{16} to 10^{17}. Thus, at most, roughly 10^{-3} to 10^{-2} of the intersecting chains are inferred to have been broken. A similar result was obtained by Backman and DeVries for sliced polyethylene surfaces (*11*); some 10^{12} to 10^{13} radicals/cm^2 were detected on surfaces expected to exhibit some 10^{14} to 10^{15} intersections/cm^2.

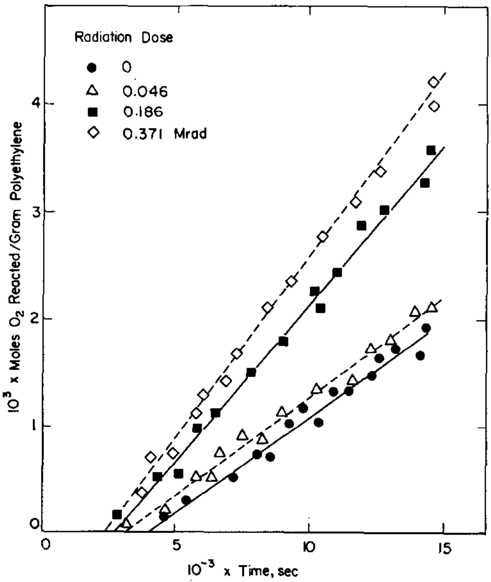

FIG. 3. Effect of irradiation of polyethylene on the uptake of oxygen during Tetralin oxidation at 65°C.

All these results are broadly consistent with accepted models of the morphology and fracture of semicrystalline polymers (*6*). The morphological model shown in Fig. 2b consists of ribbon-like crystals in which the chains traversing a crystal are normally folded back on themselves, reentering the crystal. A small fraction of the chains, however, interconnect the adjacent crystals. The value to be assigned to this fraction is ill defined, but could well be about 10^{-3} to 10^{-2} for polymers like ours, crystallized at temperatures slightly below the melting point. Electron microscopy of fracture surfaces shows clearly that fracture normally propagates though these sparse intercrystalline areas (*12*). Hence, the formation of low concentrations of surface free radicals is explained by scission of carbon–carbon bonds in the intercrystalline domains during grinding. The decay of these radicals during aging, as inferred from the data of Fig. 1, is consistent with the ESR observations of DeVries, Roylance and Williams (*13*).

We can now suggest a sequence of elementary reaction steps to account for the observed Tetralin oxidation initiated by surface free radicals:

Initiation $R_p^{\cdot} + RH \xrightarrow{k_1} R\cdot + R_pH,$ (1)

Propagation $R\cdot + O_2 \xrightarrow{k_2} ROO\cdot,$ (2)

$ROO\cdot + RH \xrightarrow{k_3} ROOH + R\cdot,$ (3)

Termination $ROO\cdot + ROO\cdot \xrightarrow{k_4}$ inert products. (4)

All but the first step are assumed to occur homogeneously.

If we now make the steady-state approximation and assume that the concentration of $R_p^{\cdot}$ is proportional to the mass of polymer, we obtain the following expression for the steady-state rate of oxygen uptake:

$$\mathbf{r} = \mathbf{k}_3\left(\frac{\mathbf{k}_1 W}{\mathbf{k}_4}\right)^{1/2} C_{RH}{}^{3/2}. \qquad (5)$$

Taylor's observed stoichiometry for polyethylene, polypropylene, and polytetrafluoroethylene-catalyzed oxidation of Tetralin at low conversions (*1*), is in agreement with the sequence. His thorough kinetic data, obtained with polytetrafluoroethylene (*2*), agree precisely with the predicted orders of reaction in oxygen concentration and catalyst mass; the observed second-order dependence on Tetralin concentration is approximately equal to the predicted order of 3/2.

ACKNOWLEDGMENTS

We thank W. C. Neikam for assistance with the ESR experiments and G. C. A. Schuit for helpful discussions. This work was supported in part by the National Science Foundation.

REFERENCES

1. TAYLOR, W. F., *J. Catal.* **16**, 20 (1970).

2. TAYLOR, W. F., *J. Phys. Chem.* **74**, 2250 (1970).

3. TAYLOR, W. F., *J. Catal.* **27**, 193 (1972).

4. BOLLAND, J. L., *Proc. Roy. Soc. Ser. A* **186**, 220 (1946).

5. MODY, P. S., M.Ch.E. thesis, Univ. of Delaware, Newark, DE, 1973.

6. SCHULTZ, J. M., "Polymer Materials Science." Prentice-Hall, New York, 1973.

7. PALMER, R. P., AND COBBOLD, A. J., *Makromol. Chem.* **74**, 174 (1964).

8. KELLER, A., AND SAWADA, S., *Makromol. Chem.* **74**, 190 (1964).

9. KAUSCH-BLECKEN VON SCHMELING, H. H., *J. Macromol. Sci. Rev. Macromol. Chem.* **4**, 243 (1970).

10. LAWTON, E. J., POWELL, R. S., AND BALWIT, J. S., *J. Polym. Sci.* **32**, 277 (1958).

11. BACKMAN, D. K., AND DEVRIES, K. L., *J. Polym. Sci., Part A-1* **7**, 2125 (1969).

12. GEIL, P. H., "Polymer Single Crystals." Wiley (Interscience), New York, 1963.

13. DEVRIES, K. L., ROYLANCE, D. K., AND WILLIAMS, M. L., *J. Polym. Sci. Part A-2*, **8**, 237 (1970).