Autoxidation of Atactic Polypropylene and Related Alkanes. Rates and Reactivities toward Peroxy Radicals

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Rates of autoxidations of atactic polypropylene, polystyrene, and several alkanes in solution initiated by azobiscyclohexanecarbonitrile were measured at 90 °C in the absence and presence of added hydroperoxide and the reactivities toward *tert*-butylperoxyl and tetralylperoxyl radicals were measured. Atactic polypropylene was found to be oxidized faster than expected from the related alkanes. On the other hand, polystyrene was quite resistant to autoxidation. The relative reactivities of secondary and tertiary hydrogens toward *t*-butylperoxyl radical were obtained as 1: 9.7 and that for primary hydrogen was estimated to be quite small. The observed reactivity of 2,2,4-trimethylpentane was much smaller than the calculated reactivity from the results of simple alkanes, whereas the observed reactivity of atactic polypropylene was higher than the calculated one. The high reactivity of atactic polypropylene for oxidation and toward peroxyl radicals was interpreted as being due to a fast intramolecular propagation. Tetralylperoxyl radical was 3.6 times as reactive as *t*-butylperoxyl radical toward both atactic polypropylene and 2,6,10,14-tetramethylpentadecane.

The oxidation of polymers by molecular oxygen is probably the most important reaction in the ageing, deterioration, and degradation of plastics, fiber, rubber, and food. This autoxidation proceeds by a radical chain mechanism, in which the chain carrying species are the peroxyl and alkoxyl radicals.[1] We have previously reported that the reactivities of atactic polypropylene and polystyrene toward *t*-butoxyl radical are considerably smaller than those of the corresponding simple model compounds.[2] The peroxyl radicals may be a more important chain carrier in the oxidation of polyolefins especially at ambient temperature. However, the relative reactivities of polyolefins and alkanes toward a specific peroxyl radical have not yet been reported. The objective of the present paper is to determine the relative reactivities of atactic polypropylene, polystyrene, and several simple low molecular weight model compounds toward *t*-butylperoxyl and 1-tetralylperoxyl radicals generated from corresponding hydroperoxide.

Experimental

Materials. Atactic polypropylene supplied by Mitsui Petrochemical Industries was first soaked in benzene at room temperature for several days and the insoluble fraction was separated by filtration. Then a soluble fraction was purified by the conventional method, using benzene and methanol as solvent and precipitant respectively. Finally it was dried to a constant weight under vacuum at room temperature. The glc analysis showed that the dried polypropylene contained little benzene or methanol. The average molecular weight of the purified polypropylene was obtained as 8400 from its intrinsic viscosity. The infrared spectrum of the purified polypropylene showed strong absorption at 975 cm^{-1}, but little absorption at 997 cm^{-1}, indicating that little isotactic polypropylene was present.[3] Polystyrene supplied by Asahi Dow Industries was purified as described previously.[2] The purified polystyrene had an intrinsic viscosity of 0.825 at 45 °C in benzene, and the number average molecular weight was 2×10^5. A monodisperse polystyrene was also used to examine the effect of the molecular weight. This polystyrene standard was obtained from Pressure Chemical Co. and was used without further purification. Decane, tridecane, 2,6,-10, 14-tetramethylpentadecane, and chlorobenzene were washed successively with acid, water, alkali and water, dried, and distilled. 2,4-Dimethylpentane, 2,2,4-trimethylpentane, and 3-methyloctane were percolated through an activated alumina column prior to use.

Commercial *t*-butyl hydroperoxide was purified by fractional distillation, 44 °C/27 mmHg, and stored over sodium carbonate. The purity determined by iodometric titration was always higher than 98%. Tetralyl hydroperoxide was prepared by air oxidation of tetralin at 50 °C and by repeated recrystallization from hexane. Azobiscyclohexanecarbonitrile (ACN) and 2,6-di-*t*-butyl-4-methylphenol (BMP) were recrystallized from methanol. Commercial oxygen and nitrogen were used as received.

Procedures. The polymer solutions were prepared by dissolving a weighed amount of polypropylene or polystyrene into chlorobenzene in a volumetric tube. All polymers dissolved completely both at room temperature and at 90 °C and the solutions were always homogeneous.

The oxidation was carried out in an ampoule immersed in a silicone oil bath carefully maintained at constant temperature ($\pm$0.02 °C). The rate of oxidation was measured either by following the pressure change using a pressure transducer or by measureing the initial and final amounts of oxygen in the reaction vessel by a Toepler pump and subsequent gas analysis by gas chromatography or Cu–CuO furnace.[4] Plots of pressure change as a function of time gave excellent straight lines without any noticeable autocatalytic or autoretarding effect at the initial stage of the oxidation. The rate of decomposition of ACN was measured from the rate of nitrogen evolution and the rate of initiation was determined from the induction period in the presence of inhibitor.[5] BMP was used as the inhibitor.

Results and Discussion

Rates of Oxidation of Atactic Polypropylene, Polystyrene, and Alkanes at 90 °C. The rates of oxidation of atactic polypropylene, polystyrene, and several alkanes initiated with ACN at 90 °C are summarized in Table 1. To obtain the rate of oxidation in the propagation step, the observed rate of oxidation was corrected for nitrogen evolution from ACN and oxygen absorption and evolution associated with initiation and termination by

$$R_{\text{prop}} = R_{\text{obsd}} + \frac{R_i}{2e} - \frac{7}{4}R_i \qquad (1)$$

where R_i is the rate of initiation and e is the efficiency of

TABLE 1. OXIDATION OF ATACTIC POLYPROPYLENE, POLYSTYRENE, AND SEVERAL ALKANES IN CHLOROBENZENE AT 90 °C

Substrate, M	[ACN] × 10^2, M	R_{prop} × 10^6, M/s	$k_p/(2k_t)^{1/2}$ × 10^3, $(Ms)^{-1/2}$
Decane, 2.57	0.996	0.55	0.32
Tridecane, 2.05	1.02	0.56	0.40
3-Methyloctane, 2.79	1.01	0.73	0.57
2,6,10,14-Tetramethylpentadecane, 1.46	1.00	1.76	1.79
2,2,4-Trimethylpentane, 3.03	1.01	0.18	0.041
Polypropylene, 0.999	2.00	1.41	1.48
Polystyrene,[a] 1.00	1.00	—0	
Polystyrene 20400,[b] 0.975	1.00	—0	

a) Polystyrene with $M_n = 2 \times 10^5$. b) Monodisperse polystyrene, $mw = 20400$ and $M_w/M_n < 1.10$.

initiation by ACN.[4] The ratio of the rate constants, $k_p/(2k_t)^{1/2}$, was calculated from the rate of oxidation by

$$k_p/(2k_t)^{1/2} = R_{prop}/[\mathrm{RH}]R_i^{1/2} \qquad (2)$$

where k_p and k_t are the rate constants for the propagation and termination reactions respectively.

Table 1 shows that $k_p/(2k_t)^{1/2}$ for tridecane is 1.25 times as large as that for decane, which corresponds well with the ratio of the number of secondary hydrogens in tridecane to that in decane, 22/16=1.38. This probably indicates that the rate constants for propagation (per active hydrogen) and termination reactions are similar for decane and tridecane. The high $k_p/(2k_t)^{1/2}$ for 2,6,10,14-tetramethylpentadecane must be ascribed to a relatively high k_p and low k_t due to the four tertiary hydrogen atoms. However, 2,2,4-trimethylpentane has an extraordinarily low $k_p/(2k_t)^{1/2}$, apparently due to the low reactivity of its tertiary hydrogen atom (see later text and Ref. 2). On the other hand, atactic polypropylene has a rather high $k_p/(2k_t)^{1/2}$. It is interesting that atactic polypropylene is as oxidizable as 2,6,10,14-tetramethylpentadecane. This may be because of a low k_t due to the tertiary alkylperoxyl radicals, but more probably because of a high k_p due to the fast intramolecular propagation. The rates of oxidation of polystyrenes were too small to permit the calculation of reliable $k_p/(2k_t)^{1/2}$. Considering that polystyrene has tertiary benzylic hydrogen, this extraordinarily low oxidizability is surprising. It may occur because of a very low reactivity of polystyrene toward oxy radicals[2] and high termination rate constants.

Oxidation with Added Hydroperoxide. Hydroperoxide is quite reactive toward peroxyl radical and therefore it is quite an efficient chain transfer agent in the autoxidation.[6] Accordingly, the addition of hydroperoxide changes the chain carrying peroxyl radical from substrate peroxyl radical to the peroxyl radical derived from the added hydroperoxide. When the added hydroperoxide (BOOH) gives a tertiary peroxyl radical ($\mathrm{BO_2}\cdot$), the termination reactions proceed as follows:[7]

$$\mathrm{BO_2}\cdot + \mathrm{BO_2}\cdot \xrightarrow{\alpha} \mathrm{BOOB} + \mathrm{O_2} \qquad (3)$$

$$\searrow_{1-\alpha}\ 2\,\mathrm{BO}\cdot + \mathrm{O_2} \qquad (4)$$

$$\mathrm{BO}\cdot + \mathrm{BOOH} \longrightarrow \mathrm{BOH} + \mathrm{BO_2}\cdot \qquad (5)$$

The alkoxyl radical generated from the non-terminating interactions of tertiary peroxyl radicals exclusively abstracts hydrogen from the hydroperoxide before it reacts with the substrate or cleaves. The rate of oxygen evolution in the termination step (R_{term}) is then given by[7]

$$R_{term} = R_i/2\alpha \qquad (6)$$

where α is the fraction of the interactions of tertiary peroxyl radicals that are terminating.

The results of the oxidations of atactic polypropylene, polystyrene, and several alkanes at 90 °C in the presence of initially added *t*-butyl and 1-tetralyl hydroperoxides

TABLE 2. OXIDATION OF ATACTIC POLYPROPYLENE, POLYSTYRENE, AND ALKANES IN CHLOROBENZENE IN THE PRESENCE OF HYDROPEROXIDE AT 90 °C

Substrate, M	[ACN] × 10^2, M	Hydroperoxide M	R_{prop} × 10^6, M/s	k_{BR}[c] $(Ms)^{-1}$	k_{TR} $(Ms)^{-1}$
Decane, 2.05	1.01	*t*-Butyl, 1.60	7.72	0.612 (0.619)	
Tridecane, 1.64	1.02	*t*-Butyl, 1.60	8.79	0.863 (0.851)	
3-Methyloctane, 2.23	1.02	*t*-Butyl, 0.80	9.12	0.658	
3-Methyloctane, 2.23	1.02	*t*-Butyl, 1.60	10.20	0.736 (0.763)	
2,6,10,14-Tetramethylpentadecane, 1.17	1.02	*t*-Butyl, 1.60	16.80	2.31 (2.02)	
2,6,10,14-Tetramethylpentadecane, 1.46	0.992	Tetralyl, 0.102	1.73		8.36
2,2,4-Trimethylpentane, 3.03	0.992	*t*-Butyl, 1.60	3.15	0.170 (0.453)	
Polypropylene, 0.717	1.00	*t*-Butyl, 1.60	4.31	0.977 (0.453)	
Polypropylene, 2.0	2.00	Tetralyl, 0.0513	1.28		3.14
Polypropylene, 2.0	2.00	Tetralyl, 0.100	1.34		3.29
Polystyrene,[a] 0.795	1.02	*t*-Butyl, 1.60	0	0 (0.453)[d]	
Polystyrene 20400,[b] 0.780	1.02	*t*-Butyl, 1.60	0	0 (0.453)[d]	

a) b) See footnote of Table 1. c) Numbers in the parentheses are k_{BR} calculated with $k_{prim} = 0$, $k_{sec} = 0.0387$, and $k_{tert} = 0.376\ \mathrm{M^{-1}\,s^{-1}}$ (see text). d) The contribution of benzyl resonance is neglected (see Ref. 2).

are summarized in Table 2. In the presence of *t*-butyl hydroperoxide, the rate of oxidation in the propagation step was obtained by correcting the observed rate of gas absorption for nitrogen evolution from ACN and oxygen absorption and evolution associated with the initiation and termination steps by

$$R_{\mathrm{prop}} = R_{\mathrm{obsd}} + \frac{R_{\mathrm{i}}}{2e} - R_{\mathrm{i}} + \frac{R_{\mathrm{i}}}{2\alpha} \tag{7}$$

The value of α for *t*-butylperoxyl radicals was determined from the rate of oxygen evolution in the induced decomposition of *t*-butyl hydroperoxide by ACN in chlorobenzene at 90 °C: the value of 0.059 was obtained. This shows that only 5.9% of the bimolecular interactions of *t*-butylperoxyl radicals are terminating and about 94% are non-terminating to give *t*-butoxyl radicals. It was assumed that the increase in the macroscopic viscosity due to atactic polypropylene and polystyrene had no effect on α.[8] For the oxidation with added tetralyl hydroperoxide, which gives a secondary peroxyl radical, the observed rate of gas absorption was corrected by Eq. (8) with the assumption that all the bimolecular interactions of tetralylperoxyl radicals are terminating.[9]

$$R_{\mathrm{prop}} = R_{\mathrm{obsd}} + \frac{R_{\mathrm{i}}}{2e} - \frac{R_{\mathrm{i}}}{2} \tag{8}$$

Tables 1 and 2 show that the addition of *t*-butyl hydroperoxide increased the rate of oxidation for every substrate except polystyrene. This is apparently due to a low termination rate constant for *t*-butylperoxyl radicals.[10]

The rate constant k_{BR} for the hydrogen atom abstraction from the substrate by *t*-butylperoxyl radical was calculated from Eq. (9)[6]

$$k_{\mathrm{BR}} = R_{\mathrm{prop}}/[\mathrm{RH}](R_{\mathrm{i}}/2k_{\mathrm{tBB}})^{1/2} \tag{9}$$

where k_{tBB} is the rate constant for direct termination by *t*-butylperoxyl radical.[10] The absolute termination rate constant was calculated as $2k_{\mathrm{tBB}}=1.2\times10^4\ \mathrm{M^{-1}\,s^{-1}}$ at 90 °C from the literature value,[11]

$$\log(2k_{\mathrm{tBB}}) = 9.2-8.5/2.303RT \tag{10}$$

This k_{BR} shows the reactivities of the substrate toward a *t*-butylperoxyl radical. The rate constants for hydrogen atom abstraction from primary, secondary, and tertiary carbon-hydrogen bonds by *t*-butylperoxyl radical were calculated from k_{BR} for decane, tridecane, 3-methyloctane, and 2,6,10,14-tetramethylpentadecane. The best results are $k_{\mathrm{prim}}=0$, $k_{\mathrm{sec}}=0.0387$, and $k_{\mathrm{tert}}=0.376$ $\mathrm{M^{-1}\,s^{-1}}$ (per hydrogen). The rate constant for primary hydrogen was obtained as a negative value and so is estimated as zero, since this is obtained as a small difference between large quantities and a small experimental error would produce a large error in k_{prim}. The calculated k_{BR} from the above k_{prim}, k_{sec}, and k_{tert} is also shown in Table 2. The agreement between the observed and calculated k_{BR} values is satisfactory for decane, tridecane, 3-methyloctane, and 2,6,10,14-tetramethylpentadecane. However, the observed k_{BR} for 2,2,4-trimethylpentane is much lower than the calculated k_{BR}. This lower reactivity of 2,2,4-trimethylpentane toward *t*-butylperoxyl radical must be due to its preferred conformation as observed toward *t*-butoxyl radical.[2] The observed reactivity of atactic polypropylene was larger than the calculated one by a factor of more than 2. Since atactic polypropylene also has an alternate methyl group along the main chain, the tertiary hydrogens must be sterically protected from the attack of *t*-butylperoxyl radical. The high k_{BR} for atactic polypropylene must imply the contribution of intramolecular propagation even in the presence of a high concentration of *t*-butyl hydroperoxide. On the other hand, polystyrene was found to be quite stable toward a *t*-butylperoxyl radical. This may be ascribed to a profound steric protection by phenyl groups on the alternating carbon atoms.

The oxidation of alkanes has been studied by several investigators. Allara *et al.*[12] estimated the relative reactivities of primary, secondary, and tertiary hydrogens toward peroxyl radicals as 1: 10: 80 at 100 °C. In the oxidation of isobutane, primary hydrogen was found to be stable and only tertiary hydrogen was oxidized selectively.[13] Mill *et al.*[14] obtained the relative reactivities of primary and secondary hydrogens as 1: 45 in the oxidation of butane at 100 °C. On the other hand, Van Sickle *et al.*[15] reported that the ratio of attack by peroxyl radicals at primary and secondary hydrogens was 1: 38.5 in the oxidation of pentane at 100 °C. Bennett, Brown, and Mile[16] measured the relative reactivities of primary, secondary, and tertiary hydrogens by product analyses in the oxidation of 2-methylpentane and obtained the ratio of 1: 18: 133 at 20 °C. Some of these relative reactivities are not toward a specific peroxyl radical but toward composite peroxyl radicals and, in some cases, the contribution of an alkoxyl radical is also possible.

From Table 2, the relative reactivities of secondary and tertiary hydrogens toward *t*-butylperoxyl radical is obtained as $k_{\mathrm{sec}}:k_{\mathrm{tert}}=1:9.7$. This is in satisfactory agreement with the literature value shown above. Since the relative reactivities of primary, secondary, and tertiary hydrogens toward *t*-butoxyl radical was 0.14: 1: 2.9 at 45 °C,[2] *t*-butylperoxyl radical is more selective than *t*-butoxyl radical, as was expected.

Bennett, Eyre, and Summers[17] measured the absolute termination rate constant in the oxidation of 2,6,10,14-tetramethylpentadecane and obtained $2k_{\mathrm{t}}=3.0\times10^6$ $\mathrm{M^{-1}\,s^{-1}}$ at 88 °C. With this $2k_{\mathrm{t}}$ and $k_{\mathrm{p}}/(2k_{\mathrm{t}})^{1/2}$ in Table 1, we obtain $k_{\mathrm{p}}=3.1\ \mathrm{M^{-1}\,s^{-1}}$, which is in fair agreement with k_{BR} in Table 2. The fact that k_{p} is about 30% higher than k_{BR} may be partly because of the contribution of the secondary peroxyl radicals, which are more reactive than the *t*-butylperoxyl radical.

In Table 2 is shown the effect of addition of 1-tetralyl hydroperoxide. The rate constants k_{TR} for the reactions of 1-tetralylperoxyl radical and 2,6,10,14-tetramethylpentadecane and atactic polypropylene were calculated from

$$k_{\mathrm{TR}} = R_{\mathrm{prop}}/[\mathrm{RH}](R_{\mathrm{i}}/2k_{\mathrm{tTT}})^{1/2} \tag{11}$$

where k_{tTT} is the constant for the termination reaction of 1-tetralylperoxyl radicals, which was calculated from the literature value:[18]

$$k_{\mathrm{tTT}} = 4.3\times10^9 \exp(-4300/RT) \tag{12}$$

The calculated k_{TR} are shown in Table 2. The reactivities of both atactic polypropylene and 2,6,10,14-tetramethylpentadecane toward 1-tetralylperoxyl radical are higher than those toward *t*-butylperoxyl radical. 1-Tetralylperoxyl radical is more reactive than *t*-butylperoxyl radical by a factor of 3.6. Table 2 shows, however, that the rate of oxidation in the presence of 1-tetralyl hydroperoxide is considerably lower than that in the presence of *t*-butyl hydroperoxide. This is due to a higher termination rate constant for 1-tetralylperoxyl radical (1.1×10^7 M^{-1} s^{-1} at 90 °C) than that for *t*-butylperoxyl radical (6.0×10^3).

When the rate constans k_{BR} and k_{TR} are calculated from the rate of oxidation in the presence of initially added hydroperoxide as described above (Eqs. (9) and (11)), it is required that all the chain carriers are changed from the substrate peroxyl radical to the peroxyl radical derived from hydroperoxide.[19,20] In other words, if the contribution of the substrate peroxyl radical in either the propagation or the termination step is not negligiblly small, Eqs. (9) and (11) do not hold. This complication is especially important for reactive substrates at higher temperature. However, the substrates studied in this work are much less reactive than the hydroperoxide. Moreover, the contribution of the substrate peroxyl radical in the propagation or termination step should give less error, if any, in the relative k_{BR} and k_{TR} and therefore in the relative reactivities of primary, secondary, and tertiary hydrogens.

Another complication that must be considered is the reaction of *t*-butoxyl radical in the oxidation with added *t*-butyl hydroperoxide. For Eq. (7) to hold, a *t*-butoxyl radical generated from the non-terminating interactions of *t*-butylperoxyl radicals should exclusively abstract hydrogen from *t*-butyl hydroperoxide before it reacts with the substrate or cleaves to acetone and methyl radical. It may well be concluded that this condition is satisfied in this study from the experimental data that the observed α was independent of the concentration of *t*-butyl hydroperoxide when it was higher than 0.80 M.

References

1) E. Niki, C. Decker, and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2813 (1973).

2) E. Niki and Y. Kamiya, *J. Org. Chem.*, **38**, 1403 (1973); *J. Chem. Soc., Perkin II*, in press.

3) J. P. Luongo, *J. Appl. Polym. Sci.*, **3**, 302 (1960).

4) E. Niki, Y. Takaishi, and Y. Kamiya, *Nippon Kagaku Kaishi*, **1975**, 1559.

5) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Amer. Chem. Soc.*, **77**, 3233 (1955).

6) J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Adv. Chem. Ser.*, Vol. 75, *Amer. Chem. Soc.*, (1968), p. 6.

7) J. R. Thomas, *J. Amer. Chem. Soc.*, **87**, 3835 (1965).

8) E. Niki and Y. Kamiya, *ibid.*, **96**, 2129 (1974).

9) G. A. Russell, *ibid.*, **79**, 3871 (1957).

10) J. A. Howard, *Adv. Free Radical Chem.*, **4**, 49 (1971).

11) S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).

12) D. L. Allara, D. Edelson, and K. C. Irwin, *Int. J. Chem. Kinet.*, **4**, 345 (1972).

13) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Adv. Chem. Ser.*, Vol. 76, *Amer. Chem. Soc.*, (1968), p. 40.

14) T. Mill, F. R. Mayo, H. Richardson, K. C. Irwin, and D. C. Allara, *J. Amer. Chem. Soc.*, **94**, 6802 (1972).

15) D. E. Van Sickle, T. Mill, F. R. Mayo, H. Richardson, and C. W. Gould, *J. Org. Chem.*, **38**, 4435 (1973).

16) J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.*, **66**, 386 (1970).

17) J. E. Bennett, J. A. Eyre, and R. Summers, *J. Chem. Soc., Perkin II*, **1974**, 977.

18) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **44**, 1119 (1966).

19) E. Niki, K. Okayasu, and Y. Kamiya, *Int. J. Chem. Kinet.*, **6**, 279 (1974).

20) J. A. Howard and J. B. Chenier, *ibid.*, **6**, 527 (1974).