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# Kinetic Study of the Polymerization of Styrene in the Presence of Various Organic Hydroperoxides

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The polymerizations of styrene initiated by 2,2′-azobisisobutyronitrile have been carried out in the presence of various organic hydroperoxides, scuh as 1,1-dimethylethyl ($\mathbf{I}_a$), 1,1-dimethylbutyl ($\mathbf{I}_b$), and 1-methyl-1-phenylethyl hydroperoxides ($\mathbf{I}_c$) at 60 °C. The polymerization rate increased with the concentration of $\mathbf{I}_c$;' but became rather retarded with that of $\mathbf{I}_a$ and $\mathbf{I}_b$. This phenomenon can be explained by the difference in the radical induced decomposition for the hydroperoxides. The hydroperoxide ($\mathbf{I}_c$) decomposes with a radical displacement on the peroxide bond; however, $\mathbf{I}_a$, and $\mathbf{I}_b$, in addition to this reaction, decompose with the radical hydrogen abstraction of the hydroperoxyl group. The peroxyl radical formed (ROO·) subsequently gave rise to a primary radical termination.

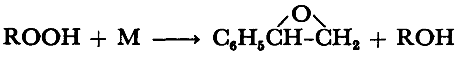
So far, many investigators have been interested in the decomposition of hydroperoxides (ROOH) which are significant substances as initiators for radical polymerization and intermediates in autoxidation processes[1] and biological systems.[2] However, the decomposition of hydroperoxides has not yet been made sufficiently clear. The decomposition mechanism of hydroperoxides is much more complicated than those of the other types of peroxides, i.e., dialkyl peroxide, diacyl peroxide and peroxyester.[3] For instance, the apparent rate constants for the decomposition reaction are considerably influenced by the structure and concentration of hydroperoxides, and on solvents.[4] This phenomenon has been attributed to the possibility that different types of decompositions occur simultaneously in the reaction. In addition to two types of homolytic radical decompositions, i.e., uni- (Eq. 1) and bimolecular decompositions (Eq. 2),

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \cdot\mathrm{OH} \qquad (1)$$

$$2\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{H_2O} + \cdot\mathrm{OOR} \qquad (2)$$

hydroperoxide decomposes with the following molecularly assisted homolysis (Eq. 3) and epoxidation (Eq. 4) in the presence of styrene (M). Furthermore,

$$\mathrm{ROOH} + \mathrm{M} \longrightarrow (\mathrm{MOH})\cdot + \mathrm{RO\cdot} \qquad (3)$$



$$\mathrm{ROOH} + \mathrm{M} \longrightarrow \mathrm{C_6H_5\overset{O}{CH\text{-}CH_2}} + \mathrm{ROH} \qquad (4)$$

two types of radical-induced decompositions (direct attack on the peroxide bond (Eq. 5) and hydrogen abstraction of the hydroperoxyl hydrogen atom (Eq. 6)), have also been postulated regarding the polymerization of styrene (N is polystyryl radical.).[3,5,6] For these reasons, the behavior of hydroperoxides in the polymerization process has not been fully understood.

$$\mathrm{N} + \mathrm{ROOH} \longrightarrow \mathrm{NON\ (polymer)} + \mathrm{RO\cdot} \qquad (5)$$

$$\mathrm{N} + \mathrm{ROOH} \longrightarrow \mathrm{NH\ (polymer)} + \mathrm{ROO\cdot} \qquad (6)$$

Quantitative information concerning the decomposition of hydroperoxides was obtained by several kinetic studies on the polymerization. Johnson and Tobolsky[7] reported apparent chain-transfer constants of 1,1-dimethylethyl ($\mathbf{I}_a$) and 1-methyl-1-phenylethyl hydroperoxides ($\mathbf{I}_c$), 0.035 and 0.063, respectively. They did not recognize any difference of polymerization activity with the structure of hydroperoxide. A retardation of the polymerization rate has been observed for a high concentration of $\mathbf{I}_a$. Walling and Heaton explained this phenomenon kinetically by assuming a chain transfer of polystyryl radical with an $\mathbf{I}_a$ dimer to yield an unreactive species.[5] In this work, we studied kinetically polymerization in the presence of hydroperoxide using 2,2′-azobisisobutyronitrile (AIBN) as an initiator at 60 °C. The homolytic and ionic decompositions of Eqs. 1—4 are minimized under this experimental condition; the hydroperoxide may be mainly consumed with radical induced decompositions of Eqs. 5 and 6, i.e., chain-transfer reactions.

## Results and Discussion

**Kinetic Scheme.** The bulk polymerization of styrene initiated by AIBN at 60 °C has been achieved in the presence of three hydroperoxides (**I**); the kinetic

$$\mathrm{ROOH} = \mathrm{R_aR_bR_cCOOH}\ (\mathbf{I})$$

$\mathbf{I}_a$: 1,1-dimethylethyl hydroperoxide ($R_a = R_b = R_c = CH_3$)
$\mathbf{I}_b$: 1,1-dimethylbutyl hydroperoxide ($R_a = R_b = CH_3$, $R_c = n\text{-}C_3H_7$)
$\mathbf{I}_c$: 1-methyl-1-phenylethyl hydroperoxide ($R_a = R_b = CH_3$, $R_c = C_6H_5$)

data are shown in Table 1. The overall scheme for the polymerization can be given as follows.

Decomposition of the initiators:

$$\mathrm{AIBN} \longrightarrow 2\mathrm{R_1} + \text{nitrogen} \quad 2f_1k_{d1}[\mathrm{AIBN}], \qquad (7)$$

where $R_1$ is $(CH_3)_2\dot{C}\text{-}CN$, $f_1$, fraction of primary radical ($R_1$) escaping from solvent cage, $k_{d1}$, decomposition constant of AIBN. Chain initiation by the hydroperoxide is based on the reaction of Eqs. 1—3; however, only the bimolecular reaction between the hydroperoxide and styrene (Eq. 3) becomes important in bulk polymerization at lower temperatures. Tobolsky and Matlack found that the rate of chain initiation ($R_i$) from hydroperoxide could be interpreted as bimolecular reactions of several types as shown in Eq. 8:[8]

$$R_i = k_{d2}[\mathrm{ROOH}][\mathrm{M}] + k'_{d2}[\mathrm{ROOH}][\mathrm{X}] \tag{8}$$

Here, X is a specific solvent, and $k_{d2}$ and $k'_{d2}$ are rate constants of bimolecular reactions, respectively. In bulk polymerization of styrene, the second term of the right-hand side in Eq. 8 can be neglected.

Chain initiation:

$$\mathrm{R}_1 + \mathrm{M} \longrightarrow \mathrm{N}_1 \qquad k_{pr1}[\mathrm{R}_1][\mathrm{M}] \tag{9}$$

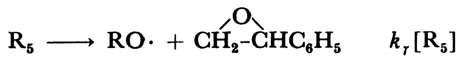
$$\mathrm{R}_2 + \mathrm{M} \longrightarrow \mathrm{N}_2 \qquad k_{pr2}[\mathrm{R}_2][\mathrm{M}] \tag{10}$$

$$\mathrm{R}_3 + \mathrm{M} \longrightarrow \mathrm{R}_5 \qquad k_{pr3}[\mathrm{R}_3][\mathrm{M}] \tag{11}$$

$$\mathrm{R}_4 + \mathrm{M} \longrightarrow \mathrm{N}_2 \qquad k_{pr4}[\mathrm{R}_4][\mathrm{M}] \tag{12}$$

$$\mathrm{R}_5 + \mathrm{M} \longrightarrow \mathrm{N}_2 \qquad k_{pr5}[\mathrm{R}_5][\mathrm{M}] \tag{13}$$

where $k_{prj}$ is rate constant for the addition of primary radical, $R_j$ ($R_2$=RO·, $R_3$=ROO·, $R_4$=(MOH)·, and $R_5$=$ROOCH_2\dot{C}HC_6H_5$) to styrene and $N_j$ is the polystyryl radical of *j* monomeric units. Walling and Heaton suggested that 60% of the 1-phenyl-2-*t*-alkylperoxyl ethyl radical ($R_5$) arising from Eq. 11 should yield styrene oxide in pure styrene at 70 °C.[5] The *γ*-scission of $R_5$ in Eq. 15 competes with the addition to styrene (Eq. 13):



$$\mathrm{R}_5 \longrightarrow \mathrm{RO}\cdot + \mathrm{CH_2\text{-}CHC_6H_5} \qquad k_\gamma[\mathrm{R}_5] \tag{15}$$

Here, $k_\gamma$ is rate constant of the *γ*-scission. The 2-cyano-2-propyl[9] and alkoxyl radicals[10] of $R_1$ and $R_2$ are very reactive against styrene, and $R_4$ and $R_5$ have the similar reactivity as polystyryl radical. The peroxyl radical of $R_3$ is most stable compared with the other radicals.

Propagation:

$$\mathrm{N}_n + \mathrm{M} \longrightarrow \mathrm{N}_{n+1} \qquad k_p[\mathrm{N}][\mathrm{M}], \tag{16}$$

where $k_p$ is propagation rate constant.

Chain transfer:

$$\mathrm{N}_n + \mathrm{M} \longrightarrow \mathrm{N}_1 + \text{polymer} \qquad k_{trM}[\mathrm{N}][\mathrm{M}], \tag{17}$$

where $k_{trM}$ is rate constant of transfer to styrene. Equations 5 and 6 are chain transfer to the hydroperoxide and the rates may be written respectively as:

$$\text{Rate of attack on the peroxide bond} = k_{trP}[\mathrm{N}][\mathrm{ROOH}] \tag{18}$$

$$\text{Rate of hydrogen abstraction} = k_{trH}[\mathrm{N}][\mathrm{ROOH}], \tag{19}$$

where $k_{trP}$ and $k_{trH}$ are the rate constants, respectively.

Termination:

$$\mathrm{N}_n + \mathrm{N}_s \longrightarrow \text{polymer} \qquad \bar{k}_t[\mathrm{N}] \tag{20}$$

$$\mathrm{N}_n + \mathrm{R}_3 \longrightarrow \text{polymer} \qquad \bar{k}_{tpr3}[\mathrm{N}][\mathrm{R}_3] \tag{21}$$

where $\bar{k}_t$ is the rate constant of termination between polymer radicals, and $k_{tpr3}$ is the rate constant of a primary radical termination between polymer and peroxyl redicals. Here, only the most stable peroxyl radical is considered to participates in a primary radical termination under these polymerization conditions.[11]

The polymerization rate is written:

$$\begin{aligned} R_p = {} & k_p[\mathrm{N}][\mathrm{M}] + k_{pr1}[\mathrm{R}_1][\mathrm{M}] + k_{pr2}[\mathrm{R}_2][\mathrm{M}] \\ & + k_{pr3}[\mathrm{R}_3][\mathrm{M}] + k_{pr4}[\mathrm{R}_4][\mathrm{M}] \\ & + k_{pr5}[\mathrm{R}_5][\mathrm{M}] \simeq k_p[\mathrm{N}][\mathrm{M}] \end{aligned} \tag{22}$$

Table 1. Polymerization of Styrene at 60 °C

| | [ROOH] / mol l$^{-1}$ | [AIBN] / mol l$^{-1}$ | [M] / mol l$^{-1}$ | $10^5R_p$ / mol l$^{-1}$ s$^{-1}$ | $\bar{n}$ |
|---|---|---|---|---|---|
| None | 0 | 0.0239 | 8.31 | 9.48 | 588 |
| | 0 | 0.01194 | 8.33 | 7.35 | 787 |
| | 0 | 0.00478 | 8.34 | 4.02 | 1332 |
| | 0 | 0.00239 | 8.34 | 2.70 | 2011 |
| $\mathbf{I}_\mathrm{a}$ | 0.240 | 0.0239 | 8.10 | 7.58 | 274 |
| | 0.192 | 0.0239 | 8.14 | 7.04 | 309 |
| | 0.192 | 0.0239 | 8.14 | 7.07 | 315 |
| | 0.0973 | 0.0239 | 8.22 | 7.90 | 412 |
| | 0.0502 | 0.0239 | 8.26 | 8.85 | 502 |
| | 0.0235 | 0.0239 | 8.29 | 8.86 | 593 |
| | 0.240 | 0.00478 | 8.13 | 4.38 | 361 |
| | 0.191 | 0.00478 | 8.17 | 4.36 | 430 |
| | 0.0957 | 0.00478 | 8.25 | 3.96 | 681 |
| | 0.0497 | 0.00478 | 8.29 | 4.00 | 942 |
| | 0.0249 | 0.00478 | 8.32 | 4.31 | 1130 |
| | 0.193 | 0 | 8.18 | 2.92 | 595 |
| $\mathbf{I}_\mathrm{b}$ | 0.193 | 0.0239 | 8.09 | 7.04 | 281 |
| | 0.1446 | 0.0239 | 8.14 | 8.08 | 327 |
| | 0.0965 | 0.0239 | 8.20 | 8.04 | 401 |
| | 0.0484 | 0.0239 | 8.25 | 8.58 | 471 |
| | 0.0239 | 0.0239 | 8.28 | 9.07 | 548 |
| | 0.239 | 0.00481 | 8.07 | 4.38 | 318 |
| | 0.191 | 0.00481 | 8.12 | 4.28 | 385 |
| | 0.1431 | 0.00481 | 8.17 | 4.36 | 446 |
| | 0.0960 | 0.00481 | 8.23 | 4.38 | 606 |
| | 0.0475 | 0.00481 | 8.28 | 4.71 | 831 |
| | 0.0241 | 0.00481 | 8.31 | 4.22 | 1081 |
| | 0.191 | 0 | 8.13 | 3.16 | 455 |
| | 0.0960 | 0 | 8.24 | 2.27 | 916 |
| | 0.0480 | 0 | 8.29 | 1.69 | 1592 |
| $\mathbf{I}_\mathrm{c}$ | 0.192 | 0.0239 | 8.03 | 10.00 | 222 |
| | 0.0962 | 0.0239 | 8.17 | 9.89 | 327 |
| | 0.0490 | 0.0239 | 8.24 | 9.33 | 424 |
| | 0.0243 | 0.0239 | 8.27 | 9.33 | 506 |
| | 0.192 | 0.00478 | 8.06 | 6.60 | 250 |
| | 0.0956 | 0.00478 | 8.20 | 5.51 | 433 |
| | 0.0499 | 0.00478 | 8.26 | 4.45 | 652 |
| | 0.192 | 0 | 8.06 | 5.74 | 260 |

The average chain length, $\bar{n}$, is written:

$$\bar{n}=\frac{k_p[\mathrm{N}][\mathrm{M}]}{\bar{k}_t[\mathrm{N}]^2+k_{trH}[\mathrm{N}][\mathrm{M}]+k_{trP}[\mathrm{N}][\mathrm{M}]+k_{tpr3}[\mathrm{N}][\mathrm{R}_3]+k_{trM}[\mathrm{N}][\mathrm{M}]} \tag{23}$$

Material balances under steady state condition give:

$$\frac{\mathrm{d}[\mathrm{R}_1]}{\mathrm{d}t}=2f_1k_{d1}[\mathrm{AIBN}]-k_{pr1}[\mathrm{R}_1][\mathrm{M}]=0 \tag{24}$$

$$\frac{\mathrm{d}[\mathrm{R}_2]}{\mathrm{d}t}=k_{d2}[\mathrm{ROOH}][\mathrm{M}]+k_{\gamma}[\mathrm{R}_5]+k_{trP}[\mathrm{N}][\mathrm{ROOH}]-k_{pr2}[\mathrm{R}_2][\mathrm{M}]=0 \tag{25}$$

$$\frac{\mathrm{d}[\mathrm{R}_3]}{\mathrm{d}t}=k_{trH}[\mathrm{N}][\mathrm{ROOH}]-k_{tpr3}[\mathrm{R}_3][\mathrm{N}]-k_{pr3}[\mathrm{R}_3][\mathrm{M}]=0 \tag{26}$$

$$\frac{\mathrm{d}[\mathrm{R}_4]}{\mathrm{d}t}=k_{d2}[\mathrm{ROOH}][\mathrm{M}]-k_{pr4}[\mathrm{R}_4][\mathrm{M}]=0 \tag{27}$$

$$\frac{\mathrm{d}[\mathrm{R}_5]}{\mathrm{d}t}=k_{pr3}[\mathrm{R}_3][\mathrm{M}]-k_{\gamma}[\mathrm{R}_5]-k_{pr5}[\mathrm{R}_5][\mathrm{M}]=0 \tag{28}$$

$$\frac{\mathrm{d}[\mathrm{N}]}{\mathrm{d}t}=k_{pr1}[\mathrm{R}_1][\mathrm{M}]+k_{pr2}[\mathrm{R}_2][\mathrm{M}]+k_{pr4}[\mathrm{R}_4][\mathrm{M}]+k_{pr5}[\mathrm{R}_5][\mathrm{M}]-k_{trH}[\mathrm{N}][\mathrm{ROOH}]-k_{trP}[\mathrm{N}][\mathrm{ROOH}]-k_{tpr3}[\mathrm{N}][\mathrm{R}_3]-\bar{k}_t[\mathrm{N}]^2 \tag{29}$$

**Polymerization Initiated by AIBN.** Data on a polymerization initiated by AIBN in the absence of hydroperoxide are analyzed by the conventional relationship between $\bar{n}$ and $R_p$.[7)]

$$\frac{1}{\bar{n}}=\frac{k_{trM}}{k_p}+\frac{\bar{k}_tR_p}{k_p^2[\mathrm{M}]^2} \tag{30}$$

Now, we obtained $k_{trM}/k_p=6\times10^{-5}$ and $\bar{k}_t/k_p^2=1130$ mol s l$^{-1}$; the former is the same value as that of Johnson and Tobolsky, the later is between 840 and 1350 mol s l$^{-1}$ in Ref. 12. The value of $f_1k_{d1}$ for AIBN was found to be $3.1\times10^{-6}$ s$^{-1}$ from the usual polymerization rate equation.[7)]

**Polymerization Initiated by Hydroperoxide.** The relationship among $R_p$, [M], and [ROOH] involving primary radical termination in the polymerization initiatedy a hydroperoxide is given by the following equation:

$$\frac{\bar{k}_tR_p^2}{k_p^2[\mathrm{M}]^3[\mathrm{ROOH}]}=2k_{d2}-\frac{2(k_{tpr3}k_{trH}/k_p^2k_{pr3})(R_p/[\mathrm{M}]^2)^2}{1+(k_{tpr3}/k_pk_{pr3})(R_p/[\mathrm{M}]^2)} \tag{31}$$

The second term of the right-hand side in Eq. 31 shows the retardation of the rate based on a primary radical termination of the peroxyl radical. The value of the left-hand side in the equation approaches $2k_{d2}$ when $(R_p/[\mathrm{M}]^2)^2$ is sufficiently close to zero. Figure 1 shows plots of ln $(\bar{k}_tR_p^2/k_p^2[\mathrm{M}]^3[\mathrm{ROOH}])$ vs. $(R_p/[\mathrm{M}]^2)^2$ using the data from this work, the references[5,13)] and the $k_{d2}$ values obtained from the intercept of the plot (Table 2). The values of $k_{d2}$ for $\mathbf{I_a}$ were found to be $6.1\times10^{-9}$ s$^{-1}$ at 60 °C and $8.4\times10^{-9}$ s$^{-1}$ at 70 °C, respectively.

The apparent chain transfer constant, $k_{trC}/k_p$, can be obtained from the conventional relationship between $\bar{n}$, $R_p$, [M], and [ROOH]:[5)]

$$\frac{k_{trC}}{k_p}=\frac{[\mathrm{M}]}{[\mathrm{ROOH}]}\left(\frac{1}{\bar{n}}-\frac{k_{trM}}{k_p}-\frac{\bar{k}_tR_p}{k_p^2[\mathrm{M}]^2}\right) \tag{32}$$

The values of $k_{trC}/k_p$ were found to be 0.048 for $\mathbf{I_a}$, 0.065 for $\mathbf{I_b}$ and 0.117 for $\mathbf{I_c}$, respectively, from the data in Table 1. The value for $\mathbf{I_a}$ is between 0.035 at 60 °C[7)] and 0.064 at 70 °C.[5)]

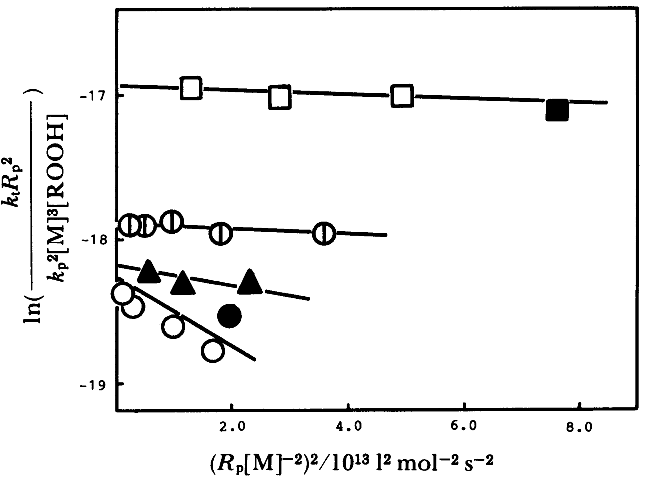


Fig. 1. Determination for chain initiation rate constants of some hydroperoxides: ○, $\mathbf{I_a}$ at 60 °C; ⦶, $\mathbf{I_a}$ at 70 °C; △, $\mathbf{I_b}$ at 60 °C; □, $\mathbf{I_c}$ at 60 °C; Closed circles, this work; Open circles, the data of references.[5,12)]

Table 2. Various Rate Constants in the Polymerization of Styrene Initiated by AIBN in the Presence of Some Hydroperoxides at 60 °C

| ROOH | $\frac{10^6f_1k_{d1}}{\mathrm{s}^{-1}}$ | $\frac{10^9k_{d2}}{\mathrm{s}^{-1}}$ | $\frac{k_{trH}}{k_p}$ | $\left(\frac{k_{trP}+2k_{trH}}{k_p}\right)$ | $\frac{k_{trP}}{k_p}$ | $\frac{10^8\,k_{pr3}k_{trH}/k_{tpr3}}{\mathrm{l\,s\,mol^{-1}}}$ | |
|---|---|---|---|---|---|---|---|
| | | | | | | From Eq. 34. | From Eq. 36. |
| $\mathbf{I_a}$ | 2.3 | 6.1 | 0.025 | 0.09 | 0.040 | 1.2 | 1.7 |
| $\mathbf{I_b}$ | 2.3 | 6.4 | 0.028 | 0.11 | 0.054 | 1.4 | 1.8 |
| $\mathbf{I_c}$ | 2.3 | 22 | 0 | 0.117 | 0.117 | — | — |

**Polymerization Initiated by AIBN in the Presence of Hydroperoxide.** The relationship among $R_p$, [M], [AIBN], and [ROOH] in the polymerization initiated by AIBN in the presence of ROOH is

$$\frac{\bar{k}_t R_p^2}{k_p^2[\mathrm{M}]^2[\mathrm{AIBN}]} = 2f_1k_{d1} + 2\left(k_{d2}[\mathrm{M}] - \frac{k_{trH}[\mathrm{N}]}{1+k_{pr3}[\mathrm{M}]/k_{tpr3}[\mathrm{N}]}\right) \times \frac{[\mathrm{ROOH}]}{[\mathrm{AIBN}]} \tag{33}$$

When the value of $k_{tpr3}$[N][$R_3$] is larger than that of $k_{pr3}$[$R_3$][M], because $1/(1+k_{pr3}[\mathrm{M}]/k_{tpr3}[\mathrm{N}]) \simeq (1-k_{pr3}[\mathrm{M}]/k_{tpr3}[\mathrm{N}])$, Eq. 33 becomes:

$$\frac{\bar{k}_t R_p^2}{k_p^2[\mathrm{M}]^2[\mathrm{AIBN}]} = 2f_1k_{d1} + 2\left(k_{d2}[\mathrm{M}] - \frac{k_{trH}R_p}{k_p[\mathrm{M}]} + \frac{k_{pr3}k_{trH}[\mathrm{M}]}{k_{tpr3}}\right) \times \frac{[\mathrm{ROOH}]}{[\mathrm{AIBN}]} \tag{34}$$

The second term of the right-hand side in Eq. 34 shows chain initiation by hydroperoxide which depends on the polymerization rate ($R_p$). Figures 2—4 show plots of the values of the left-hand side in Eq. 34 against [ROOH]/[AIBN] at two concentrations of AIBN. The plots give a linear line for $\mathbf{I}_c$, but two linear-like curves for $\mathbf{I}_a$ and $\mathbf{I}_b$, respectively. The former increases linearly with [ROOH]/[AIBN]. However, the later remarkably decreases with [ROOH]/[AIBN] at a higher concentration of AIBN (higher polymerization rate) and distinctly shows a retardation owing to the hydroperoxide. The value of $f_1k_{d1}$ was obtained from the intercept of the curves (shown in Table 2). Furthermore, the values of $k_{trH}/k_p$ and $k_{pr3}k_{trH}/k_{tpr3}$ for $\mathbf{I}_a$ and $\mathbf{I}_b$ were estimated from Eq. 34 by a least-squares method using values of $f_1k_{d1}$ and $k_{d2}$ (also shown in Table 2). Using these values, the solid curves in Figs. 2 and 3 could be simulated using Lagrange's interpolation method. The value of $k_{d2}$ for $\mathbf{I}_c$ obtained from the slope of the staight line in Fig. 4 was found to be $1.6\times10^{-8}$ s$^{-1}$.

The relationship among $\bar{n}$, $R_p$, [M], and [ROOH] is

$$\frac{1}{\bar{n}} = \frac{k_{trM}}{k_p} + \left[\frac{k_{trP}}{k_p} + \left(\frac{2k_{tpr3}[\mathrm{N}]+k_{pr3}[\mathrm{M}]}{k_{tpr3}[\mathrm{N}]+k_{pr3}[\mathrm{M}]}\right)\frac{k_{trH}}{k_p}\right]\frac{[\mathrm{ROOH}]}{[\mathrm{M}]} + \frac{\bar{k}_t R_p}{k_p^2[\mathrm{M}]^2} \tag{35}$$

The second term of the right-hand side in Eq. 35 exhibits a dependence on the chain length for chain transfers to hydroperoxide and the primary radical termination of the peroxyl radical. This term changes

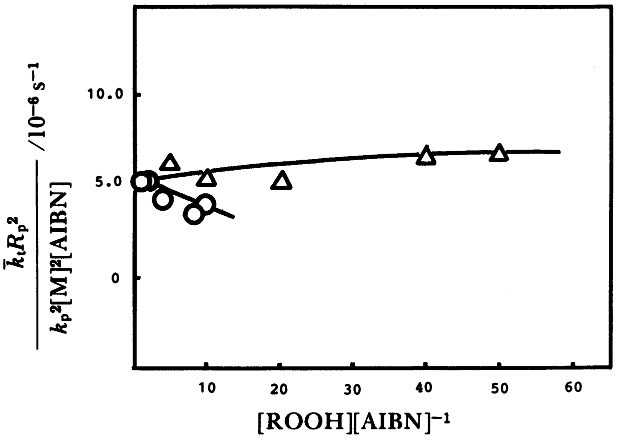


Fig. 2. Application of Eq. 34 to the data in the polymerization of styrene initiated by AIBN in the presence of $\mathbf{I}_a$ at 60 °C: Δ, [AIBN]=0.0048; O, [AIBN]=0.0239 mol l$^{-1}$; ——, Curves calculated by Lagrange's interpolation method, using the values of Table 2.

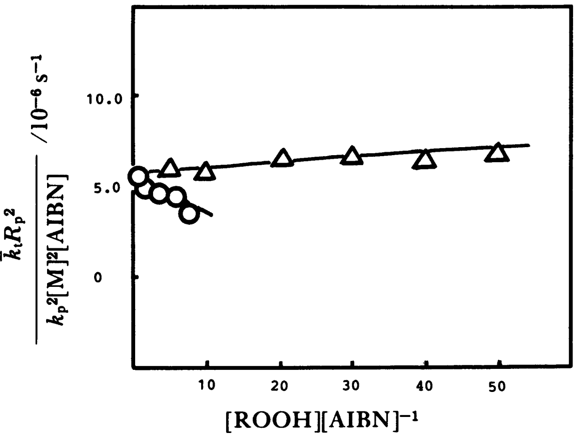


Fig. 3. Application of Eq. 34 to the data in the polymerization of styrene initiated by AIBN in the presence of $\mathbf{I}_b$ at 60 °C: Δ, [AIBN]=0.0048; O, [AIBN]=0.0239 mol l$^{-1}$; ——, Curves calculated by Lagrange's interpolation method, using the values of Table 2.

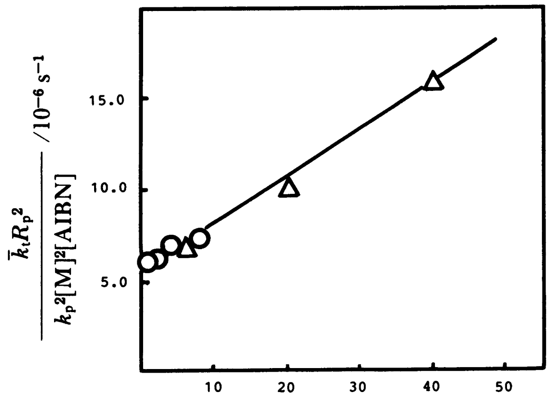


Fig. 4 A plot of $\bar{k}_tR_p^2/k_p^2[\mathrm{M}]^2[\mathrm{AIBN}]$ vs. [ROOH]/[AIBN] for the polymerization of styrene initiated by AIBN in the presence of $\mathbf{I}_c$ at 60 °C: Δ, [AIBN]=0.0048: O, [AIBN]=0.0239 mol l$^{-1}$.

largely with the relationship between $k_{tpr3}[N][R_3]$ and $k_{pr3}[M][R_3]$. When the value of $k_{tpr3}[N][R_3]$ is larger than that of $k_{pr3}[M][R_3]$, because $(2k_{tpr3}[N]+k_{pr3}[M]/(k_{tpr3}[N]+k_{pr3}[M])\simeq(2-k_{pr3}[M]/k_{tpr3}[N])$, Eq. 35 becomes:

$$\frac{1}{\bar{n}} = \frac{k_{trM}}{k_p} + \left(\frac{k_{trP}+2k_{trH}}{k_p} - \frac{k_{pr3}k_{trH}[M]^2}{k_{tpr3}R_p}\right)\frac{[ROOH]}{[M]} + \frac{\bar{k}_tR_p}{k_p{}^2[M]^2} \qquad (36)$$

When $k_{tpr3}[N][R_3] \leqslant k_{pr3}[R_3][M]$, the value of $(2k_{tpr3}[N]+k_{pr3}[M])/(k_{tpr3}[N]+k_{pr3}[M])$ changes slightly with the value of $k_{pr3}[M]/k_{tpr3}[N]$: For example, it is 1.5 when $k_{pr3}[M]=k_{tpr3}[N]$, and 1.0 when $k_{pr3}[M] \gg k_{tpr3}[N]$. The values of $(1/\bar{n}-k_{trM}/k_p-\bar{k}_tR_p/k_p{}^2[M]^2)[M]/[ROOH]$ rearranged from Eq. 36 are plotted against $1/R_p$ for $\mathbf{I_a}$ and $\mathbf{I_b}$ in Figs. 5. and 6, respectively. The figures show that the value of $(1/\bar{n}-k_{trM}/k_p-\bar{k}_tR_p/k_p{}^2[M]^2)[M]/[ROOH]$ decreases with increasing $1/R_p$ and aproaches to a nearly constant value near the value of $3.0\times10^4$ l s mol$^{-1}$ where $k_{tpr3}[N]\simeq k_{pr3}[M]$. The values of $(k_{trP}+2k_{trH})/k_p$ and $k_{pr3}k_{trH}/k_{tpr3}$ are estimated from the intercept and slop of Figs. 5 and 6 (Table 2). The value of $(1/\bar{n}-k_{trH}/k_p-\bar{k}_tR_p/k_p{}^2[M]^2)[M]/[ROOH]$ for $\mathbf{I_c}$ is constant against $1/R_p$ and the value of $(k_{trP}+2k_{trH})/k_p$ was found to be 0.117. The values of $k_{trP}/k_p$ were calculated using the data in Table 2.

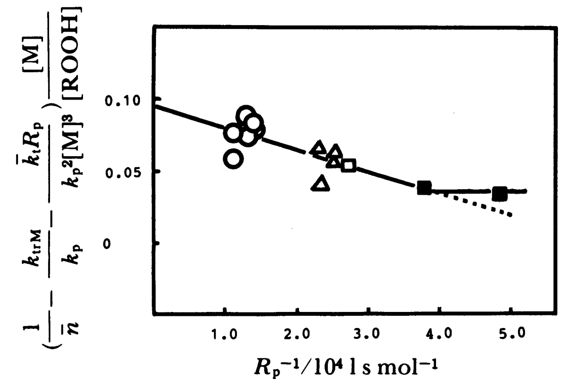


Fig. 5. Application of Eq. 36 to the data in the polymerization of styrene initiated by AIBN in the presence of $\mathbf{I_a}$ at 60 °C: □, [AIBN]=0; ■, [AIBN]=0 (the data of Baysal and Tobolsky[13]); △, [AIBN]=0.0048; ○, [AIBN]=0.0239 mol l$^{-1}$.

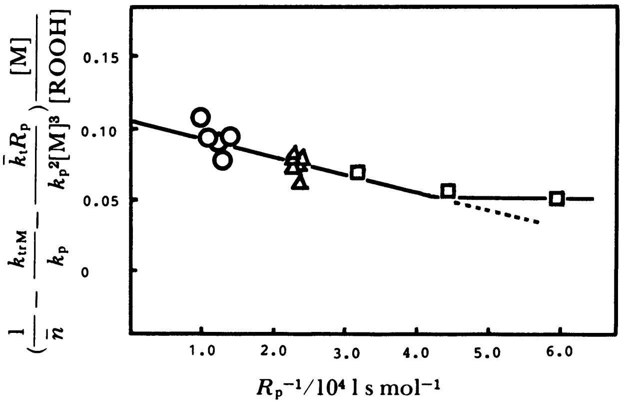


Fig. 6. Application of Eq. 36 to the data in the polymerization of styrene initiated by AIBN in the presence of $\mathbf{I_b}$ at 60 °C: □, [AIBN]=0; △, [AIBN]=0.0048; ○, [AIBN]=0.0239 mol l$^{-1}$.

Table 2 summarizes the rate constants in the polymerization of styrene initiated by AIBN in the presence of hydroperoxide at 60 °C. The same values of $f_1k_{d1}$ for three hydroperoxides agree with those for a polymerization initiated only by AIBN. The values of $k_{d2}$ and $k_{trP}/k_p$ for $\mathbf{I_c}$ are larger than those of $\mathbf{I_a}$ and $\mathbf{I_b}$. The value of $k_{trP}/k_p$ for $\mathbf{I_a}$ agrees reasonably well with 0.39 of $k_{trC}/k_p$ for 1,1-dimethylethyl deuterioperoxide,⁵⁾ which hardly seemed to undergo a deuterium abstraction reaction of the deuterioperoxyl group. The value of $k_{trH}/k_p$ for $\mathbf{I_a}$ is almost similar to that of $\mathbf{I_b}$, but is very different with that of $\mathbf{I_c}$. The values of $k_{pr3}k_{trH}/k_{tpr3}$ for $\mathbf{I_a}$ are almost similar to those of $\mathbf{I_b}$ in the cases in Eqs. 34 and 36; the values obtained from Eq. 34 are approximately equal to those from of Eq. 36. The values of $k_{pr3}k_p/k_{tpr3}$ calculated from the data in Table 2 were found to be in the range 5 to $7\times10^{-7}$ l s mol$^{-1}$. These values are hardly influenced by the structure of the hydroperoxides and are much smaller than those of benzoyl peroxide and AIBN at 60 °C.[14] The bimolecular reaction between radicals is diffusion controlled; this result indicates that the rate constant ($k_{pr3}$) for the addition of the *t*-alkylperoxyl radical to styrene is one to six-hundredth as large as those of the primary radicals from benzoyl peroxide and AIBN. In fact, a rate constant of 1.3 l mol$^{-1}$ s$^{-1}$ for the addition of the 1,1-dimethylethylperoxyl radical to styrene at 30 °C was reported[15] to be much smaller than 55 mol$^{-1}$ s$^{-1}$ of the polystyryl radical. The ratio of the addition to styrene against the primary radical termination for *t*-alkylperoxyl radical was found to be in the range 0.3 to 1.2 in this work. Thus, the unexpected behavior of $\mathbf{I_a}$ and $\mathbf{I_b}$ may be sufficiently explained by the usual primary radical termination between polymer and peroxyl radicals[14] without assuming a chain transfer with the hydroperoxide dimer to yield unreactive species.[5] The phenomenon of inhibition and retardation in polymerization by traces of molecular oxygen may also be explained by the termination between the polymer radical and the peroxyl radical formed.[16]

In conclusion, the rates of the styrene-assisted homolysis and the radical displacement reaction on the peroxide bond of the hydroperoxides are considerably influenced by the structure of hydroperoxides, and the oders in the both reactions: $\mathbf{I_c} \gg \mathbf{I_b} > \mathbf{I_a}$.[17] A radical hydrogen abstraction reaction by polystyryl radical was observed for *t*-alkyl hydroperoxides ($\mathbf{I_a}$ and $\mathbf{I_b}$), but not for α-aryl-substituted *s*-alkyl hydroperoxides ($\mathbf{I_c}$).

## Experimental

**Materials.** The commercial products of **I**$_a$ and **I**$_b$ from Nippon Oil & Fats Co., Ltd. were distilled under reduced pressure. The commercial product of **I**$_c$ from Nippon Oil & Fats Co., Ltd. was purified by isolation of the sodium salt, regeneration of the hydroperoxide by carbon dioxide and vacuum distillation. The distilled materials were shown to be 97—99% pure by iodometric titration. The commercial product of AIBN was purified by recrystallization. Styrene was fractionated under reduced pressure, stored at −20 °C and used within 24 h.

**Procedure.** Styrene and initiators were put in a glass ampoule and degassed under reduced pressure by the freeze-thaw technique. The polymerization of styrene was carried out at 60.0±0.2 °C. The conversions were estimated by gel permeation chromatography (GPC). Ultimate conversions were less than 10%. The average molecular weight of polymer was estimated by GPC.

### References

1) L. F. Martin, "Organic Peroxide Technology," Noyes Data Corporation, New Jersey (1973).

2) W. A. Pryor, "Free Radicals in Biology Vol. I," ed by W. A. Pryor, Academic Press, New York (1976), Chap. 1.

3) R. Hiatt, "Organic Peroxides Vol. II," ed by D. Swern, John Wiley & Sons, Inc., New York (1971), Chap. 1.

4) R. Hiatt and K. C. Irwin, *J. Org. Chem.*, **33**, 1436 (1968).

5) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 38 (1965).

6) C. Walling and Y. Chang, *J. Am. Chem. Soc.*, **76**, 4878 (1954).

7) D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.*, **74**, 938 (1952).

8) A. V. Tobolsky and L. R. Matlack, *J. Polym. Sci.*, **55**, 49 (1961).

9) K. Ito, *J. Polym. Sci.*, **15**, 1759 (1977).

10) (a) M. V. Encina, M. Rivera, and E. A. Lisi, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1709 (1978); (b) P. C. Wong, D. Griller, and J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 5106 (1982).

11) K. Matsuyama, T. Komai, and K. Ito, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2425 (1986).

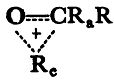
12) G. R. Ham, "Vinyl Polymerization Vol. I, Part I," ed by G. E. Ham, Marcel Kekker, Inc., New York (1967), p. 15.

13) B. Baysal and A. V. Tobolsky, *J. Polym. Sci.*, **8**, 529 (1952).

14) P. C. Deb and G. Meyerhoff, *Eur. Polym. J.*, **10**, 709 (1974); The values of $k_{pr3}k_p/k_{tpr3}$ for benzoyl peroxide and AIBN at 60 °C were reported in this reference to be $1.1\times10^{-5}$ and $4.9\times10^{-5}$ l s mol$^{-1}$, respectively.

15) J. A. Howard, *Can. J. Chem.*, **50**, 2298 (1972).

16) Ref. 12, p. 186.

17) The orders in the reactions may be explained by considering the following structures at transition state containing a nonclassical bridged component; [M (or N) $\mathrm{HO\cdot\ \cdot O{-}CR_aR_bR_c} \longleftrightarrow$ M (or N) $\mathrm{HO^-}$  $\underset{\overset{+}{\mathrm{R_c}}}{\mathrm{O{=}CR_aR_b}}$ $\longleftrightarrow \mathrm{M^+}$ (or $\mathrm{N^+}$) $\mathrm{HO^-\ \cdot O{-}CR_aR_bR_c}$].