

Reactivities of Polystyrene and Polypropylene toward t-Butoxyl Radical. Effects of Molecular Weight, Solvent, and Temperature

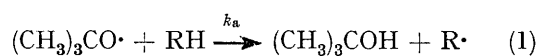
By Etsuo Niki* and Yoshio Kamiya, Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo 113, Japan

The effects of molecular weight, solvent, and temperature on the reactivities of polystyrene, polypropylene, and several simple model compounds toward t-butoxyl radical in benzene solution have been measured. The reactivity of polystyrene decreased with increasing molecular weight. When solubility was decreased by addition of acetic acid, the relative reactivities of polystyrene and polypropylene decreased significantly more than those of simple hydrocarbons. On the other hand, the reactivities of the polymers, especially of polystyrene, increased more than simple hydrocarbons with increasing temperature. The results are interpreted in terms of the coiled configuration of polymers in solution.

HYDROGEN atom abstraction by peroxy and alkoxy radicals is one of the important rate-determining elementary reactions in the oxidation of polymers.¹⁻³ We have shown previously that polystyrene and polypropylene are less reactive toward t-butoxyl radical than simple model compounds.⁴ The low reactivities were ascribed mainly to the coiled configurations of these polymers in solution. The objective of the present paper is to elucidate the effects of molecular weight, solvent, and temperature on the reactivities of polystyrene and polypropylene toward t-butoxyl radical. Di-t-butyl peroxyoxalate (DBPO) and di-t-butyl peroxide were used as t-butoxyl radical sources at 45 and 125° respectively.

RESULTS AND DISCUSSION

The finding that the reactivities of polystyrene and polypropylene toward t-butoxyl radical were lower than for model compounds⁴ has led us to examine first the effect of molecular weight on the reactivity of polystyrene. t-Butoxyl radicals may abstract a hydrogen atom from the substrate forming t-butyl alcohol [reaction (1)] or decompose forming acetone [reaction (2)].



The relative reactivities of different substrates can be estimated from the ratio of the rate constants k_a and k_d calculated from the plots of the product ratio t-butyl alcohol:acetone as a function of substrate concentration.⁴ The initial concentration of the substrates was varied in benzene solution over the range of 0—ca. 2M. Table 1 summarizes the results obtained for several monodisperse polystyrene standards in benzene at 45°. Table 1 clearly shows that the reactivity of polystyrene decreases with increasing molecular weight.

β -Scission of t-butoxyl radical may be reversible and the rate of reaction (2) may possibly be lowered in

highly viscous polymer solutions. Under these circumstances, the observed reactivity of the substrates should be higher, however it was found experimentally that the reactivity of simple hydrocarbons was independent of

TABLE I

Effect of molecular weight on the reactivity of polystyrene toward t-butoxyl radical at 45° in benzene

| Molecular weight | $[\eta]^a$ | \bar{M}_w/\bar{M}_n | k_a/k_d |
|----------------------|------------|-----------------------|-----------|
| 2 100 | 0.031 | 1.10 | 0.904 |
| 4 000 | 0.046 | 1.10 | 0.686 |
| 10 000 | 0.095 | 1.06 | 0.338 |
| 20 400 | 0.14 | 1.06 | 0.211 |
| 200 000 | 0.65 | 1.06 | 0.208 |
| 200 000 ^b | 0.825 | | 0.186 |
| 498 000 | 1.50 | 1.20 | 0.175 |

^a Intrinsic viscosity measured at 45°, in benzene. ^b Viscosity average molecular weight. This polymer has a wide molecular weight distribution. Data are from ref. 4.

the presence or absence of polystyrene in solution. A plot of t-butyl alcohol:acetone as a function of polystyrene concentration gave a satisfactory straight line without noticeable downward-convex curvature. Thus it may be concluded that the change in viscosity of the solution has little effect on the reactivity of the substrate toward t-butoxyl radical. This must be because the macroscopic viscosity has little effect on the mobility of t-butoxyl radical.⁵

To examine the effect of solvent, the reactivities of polystyrene and polypropylene were measured in benzene solution containing 20% v/v acetic acid, a poor solvent for both polymers. Under the reaction conditions employed both polymers dissolved and the solutions were always homogeneous. Some quantitative thermodynamic criterion may be preferable to show the solubility in the mixed solvent but it can be assumed to be poorer than pure benzene since both polymers did not dissolve in acetic acid and the intrinsic viscosity in the mixed solvent was less than that in pure benzene: for example the intrinsic viscosities of polystyrene

¹ E. Niki, C. Decker, and F. R. Mayo, *J. Polymer Sci. Polymer Chem.*, 1973, **11**, 2813.

² C. Decker and F. R. Mayo, *J. Polymer Sci. Polymer Chem.*, 1973, **11**, 2847.

³ C. Decker, F. R. Mayo, and H. Richardson, *J. Polymer Sci. Polymer Chem.*, 1973, **11**, 2879.

⁴ E. Niki and Y. Kamiya, *J. Org. Chem.*, 1973, **38**, 1403.

⁵ E. Niki and Y. Kamiya, *J. Amer. Chem. Soc.*, 1974, **96**, 2129, and papers cited therein.

20 400 (Table 2) were 0.141 and 0.134 in pure benzene and in the mixed solvent respectively. The results are summarized in Table 2. In the presence of acetic acid,

TABLE 2

Decomposition of di-*t*-butyl peroxyoxalate at 45° in benzene-acetic acid (20% v/v) solution

| Substrate | $(k_a/k_d)_{20\% \text{ AcOH}}$ | $(k_a/k_d)_{\text{no AcOH}}^a$ | $\frac{(k_a/k_d)_{20\% \text{ AcOH}}}{(k_a/k_d)_{\text{no AcOH}}}$ |
|---------------------------------|---------------------------------|--------------------------------|--|
| <i>t</i> -Butylbenzene | 0.31 | 1.40 | 0.22 |
| 2,2,4-Trimethylpentane | 0.49 | 2.13 | 0.23 |
| Polypropylene | 0.12 | 0.98 | 0.12 |
| Polystyrene 20 400 ^b | 0.029 | 0.211 | 0.14 |

^a In benzene without acetic acid; data from ref. 4. ^b Polystyrene with molecular weight of 20 400.

small amounts of isobutene were observed, which must be formed by dehydration of *t*-butyl alcohol. However, this amount was so small compared with the observed *t*-butyl alcohol that it could be neglected in calculations. For every substrate the ratio k_a/k_d is smaller in the presence of 20% v/v acetic acid than in its absence as predicted from the findings of Walling and Wagner⁶ that polar solvents give a higher value for k_d while k_a is relatively solvent insensitive. Although the accuracy of k_a/k_d is poorer in the presence of acetic acid owing to the low values, Table 2 shows that the decrease in k_a/k_d by the addition of acetic acid is approximately twice as large for polypropylene and polystyrene as for *t*-butylbenzene and 2,2,4-trimethylpentane.

To examine the effect of temperature, the relative reactivities of several substrates toward *t*-butoxyl radical were measured at 125°. Di-*t*-butyl peroxide was used as radical source and chlorobenzene as solvent instead of benzene. The results summarized in Table 3 show that the k_a/k_d at 125° is smaller than that at 45°. This is partly due to a solvent effect but due mainly to a higher activation energy of β -scission as compared with hydrogen atom abstraction. The ratio of k_a/k_d at 125° to that at 45° should depend on the numbers of primary, secondary, and tertiary hydrogen atoms and on the entropy factor. That this ratio for *t*-butylbenzene is larger than that for 2,3-dimethylbutane must be ascribed to the type of hydrogen atoms: 2,3-dimethylbutane has primary and tertiary hydrogens but *t*-butylbenzene is composed only of primary hydrogens. As discussed previously,⁴ the reactivities of 2,4-dimethylpentane and 2,2,4-trimethylpentane are lower than those of other saturated hydrocarbons due to the preferred conformation. However, this effect may be less important at higher temperature and in fact the observed ratios of k_a/k_d at 125° to that at 45° for these compounds are relatively larger than, for example, for 2,3-dimethylbutane. This is most significant for the polymers;

⁶ C. Walling and P. Wagner, *J. Amer. Chem. Soc.*, 1964, **86**, 3368.

polystyrene has the lowest reactivity at 45° but highest at 125° among the substrates studied in Table 3.

The results on the effects of molecular weight, solvent, and temperature on the reactivities of polystyrene and polypropylene toward *t*-butoxyl radical indicate that the specific coiled configurations of polymers in solution

TABLE 3

Relative reactivities toward *t*-butoxyl radical at 125° in chlorobenzene

| Substrate | $(k_a/k_d)_{125^\circ}$ | $(k_a/k_d)_{45^\circ}^a$ | $\frac{(k_a/k_d)_{125^\circ}}{(k_a/k_d)_{45^\circ}}$ |
|------------------------|-------------------------|--------------------------|--|
| 2,3-Dimethylbutane | 0.294 | 7.29 | 0.040 |
| 2,4-Dimethylpentane | 0.295 | 4.30 | 0.069 |
| <i>t</i> -Butylbenzene | 0.175 | 1.40 | 0.125 |
| 2,2,4-Trimethylpentane | 0.270 | 2.13 | 0.13 |
| Polypropylene | 0.248 | 0.98 | 0.25 |
| Polystyrene 4000 | 0.500 | 0.686 | 0.73 |

^a In benzene at 45°, data from ref. 4.

play an important role in determining the reactivities. No simple quantitative correlation between molecular weight and reactivity could be obtained. The higher molecular weight polystyrenes probably have lower reactivities because a smaller fraction of abstractable hydrogens is exposed to the *t*-butoxyl radicals. In poor solvents the polymer molecule adopts a tightly coiled configuration as opposed to the expanded coiled configuration in good solvents. This is why the addition of acetic acid, a poor solvent for both polystyrene and polypropylene, decreased the reactivities of these two polymers more than simple hydrocarbons. The effect of temperature implies that the entropy factor makes a significant contribution on the reactivities especially for polystyrene: at higher temperature the polymer coil must be more expanded and favours the attack of *t*-butoxyl radical. Table 3 suggests a contribution by benzyl resonance for polystyrene, which was assumed to be negligible at 45° in benzene.⁴

EXPERIMENTAL

Materials.—The purification of polypropylene and polystyrene has been described elsewhere.⁴ Standard polystyrenes with a small molecular weight distribution were obtained from Pressure Chemical Co. DBPO was prepared and purified by the method of Bartlett *et al.*⁷ Di-*t*-butyl peroxide was supplied from Nippon Oils and Fats Co. Organic solvents were commercial materials, purified if necessary by conventional methods.

Procedures.—DBPO and di-*t*-butyl peroxide were decomposed in a sealed ampoule under vacuum or oxygen-free nitrogen. The atmosphere had no effect on the decomposition rate and products. DBPO was decomposed completely in *ca.* 10 half-lives, the half-life being 41 min at 45°. The reaction mixture was analysed as described previously.⁴

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⁷ P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **82**, 1762.