the sample above) 109–109.5°. However, the phenol was different by nmr (CDCl$_3$): δ 1.00 (3 H, s), 2.05 (3 H, s), 2.40 (2 H, q, J = 7 Hz), 6.4–7.0 (3 H, m, main peak at 6.62) and was slightly separated by vpc (SE-30 on Chromosorb G) from the rearrangement product above, and its nmr signals were well separated by Eu(fod)$_3$.

Rearrangement of 4-Methyl-4-phenylcyclohexa-2,5-dienone (IIc). The dienone IIc (kindly supplied by Dr. V. P. Vitullo) has the following nmr spectrum (CCl$_4$): δ 1.75 (3 H, s), 6.50 (2 H, d, J = 10 Hz), 7.20 (2 H, d, J = 10 Hz), 7.59 (5 H, s). After 1 hr, rearrangement was complete and the product, 4-methyl-3-phenylphenol (VIIIc), was isolated in the usual way. It had nmr (CCl$_4$): δ 2.25 (3 H, s), 6.8–7.4 (3 H, m), 7.58 (5 H, s).

Treatment of 127 mg of 4-methyl-3-phenylphenol with 150 mg of NaH and 5 ml of MeI in 30 ml of DMF and refluxing 1 hr gave the methyl ether (XIb): nmr (CCl$_4$) δ 2.16 (3 H, s), 3.73 (3 H, s), 6.7–7.3 (3 H, m), 7.32 (5 H, s). It was shown by the use of Eu(fod)$_3$ that the compound contained no detectable amount of the isomer Xe (*vide supra*). Refluxing of the crude product with 500 mg of KMnO$_4$ in 10 ml of 1 N NaOH for 4 hr followed by acidification with dilute H$_2$SO$_4$ gave white crystals which were collected by filtration to yield 20 mg of 4-methoxy-2-phenylbenzoic acid, mp 170–173° (HOAc–H$_2$O) (lit.[28] 169–173°). 3-Methoxy-6-phenylbenzoic acid has mp 136–137°.[28]

Kinetic Runs. Trifluoroacetic acid was freshly distilled from P$_2$O$_5$ and stored in an oil bath at 38.5°, the temperature of the nmr probe. The probe temperature was determined using the shift of the OH proton signal of a standard methanol sample, and by observing no breaks in the plot when two identical samples of either IIb or Ia in CF$_3$COOH were switched back and forth from the bath to the probe twice during a kinetic run. Methylene chloride (3% v/v) was added as an internal standard, and absorbed at δ 5.27. To a 50-mg sample of each dienone in a preheated nmr tube was added 0.5 ml of the trifluoroacetic acid *via* preheated syringe, the tube was sealed with a pressure cap and shaken well, and the nmr spectrum in the δ 5.2–6.6 region was scanned on a Varian A-60 nmr spectrometer. *Ca.* 0.5 min elapsed before the first scan. The tube was returned to the bath when not monitored for IIa but was left in the probe for all the other dienones. The relative peak height of the larger leg of the C-3 H and C-5 H doublet of the dienone (in the δ 6.2–6.6 region for all compounds) was normalized by comparison to the CH$_2$Cl$_2$ peak and the normalized value used in kinetic plotting. A least-squares fit of the data was obtained. All runs gave good first-order kinetics, with correlation coefficients of 0.97–0.99. The average rate constants from triplicate runs are recorded in Table I.

Cage Reactions of *tert*-Butoxy Radicals. Effects of Solvent and Viscosity[1]

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Contribution from the Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo 113, Japan. Received October 18, 1973

Abstract: Cage reactions of *tert*-butoxy radicals generated by the thermal decomposition of di-*tert*-butylperoxy oxalate were studied at 45°. In the solvents of similar properties, a reciprocal of probability of geminate recombination of *tert*-butoxy radicals was a linear function of a reciprocal of viscosity of the medium in agreement with Noyes' approach. The linear correlation with identical intercepts but with different slopes depending on the nature of solvents was ascribed to a specific interaction of caged *tert*-butoxy radical with surrounding solvent molecules. The extent of interaction was suggested to be in the order of aliphatic < olefinic < aromatic < polar compounds such as acetic acid and acetonitrile, which is the same with the extent of solvent effects on the β scission of *tert*-butoxy radical observed by Walling and Wagner. However, the extent of cage reaction was low and relatively insensitive to the bulk viscosity of the solutions containing polymeric compounds. The higher the molecular weight of the dissolved polymer, the lower the extent of cage reaction at constant viscosity.

W hen a pair of radicals is produced in solution from a radical initiator such as peroxides and azo compounds, it may either diffuse out of the solvent cage or recombine within the cage. This "cage" effect has been known for many years and studied widely by numerous investigators.[2] Effects of viscosity of the medium on the geminate recombination of the paired radicals have been studied by many workers and it has been shown that the extent of cage reaction increases with increasing viscosity of the medium. The quantitative treatment developed by Noyes[3] implies that the reciprocal of probability of cage recombination is a linear function of $T^{1/2}/\eta$ where T and η denote absolute temperature and viscosity, respectively. This linear correlation was observed by Szwarc and coworkers for each solvent in the photolyses of hexafluoroazomethane[4] and azomethane.[5] Bartlett, *et al.*,[6] also observed that this correlation held in the thermal decomposition of *tert*-butylperoxy-α-phenylisobutyrate. The cage recombination of *tert*-butoxy radicals was first reported by Hiatt and Traylor,[7] who found that the yield of di-*tert*-butyl peroxide in the decomposition of di-*tert*-butylperoxy oxalate (DBPO) increased with increasing viscosity of the solution. Kiefer and Traylor[8] and

(1) Presented at the 28th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1, 1973.

(2) T. Koenig and H. Fischer, "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 4.

(3) R. M. Noyes, *Progr. React. Kinet.*, **1**, 129 (1961).

(4) O. Dobis, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 278 (1968); K. Charkravorty, J. M. Pearson, and M. Szwarc, *Int. J. Chem. Kinet.*, **1**, 357 (1969).

(5) K. Chakravorty, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 283 (1968).

(6) F. E. Herkes, J. Friedman, and P. D. Bartlett, *Int. J. Chem. Kinet.*, **1**, 193 (1969).

(7) R. Hiatt and T. G. Traylor, *J. Amer. Chem. Soc.*, **87**, 3766 (1965).

(8) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967).
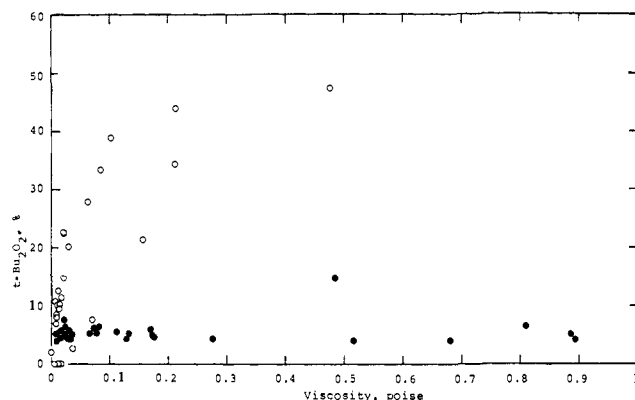
Figure 1. Viscosity effect on the cage recombination of *tert*-butoxy radicals at 45°.

Neuman and Bussey[9] have also observed the similar effects. However, these authors did not find a simple correlation between the viscosity of the solution and the extent of cage reaction. In addition to Noyes approach,[3] the alternative models have been developed by Eirich, *et al.*,[10a] and Koenig,[10b] which predict square root dependence on the fluidity ($1/\eta$) of the solution. Recently, Pryor and coworkers[11] correlated the rate of homolysis of radical initiators with viscosity. The correlation between the extent of cage reaction and viscosity is complicated and is not really settled yet.[2] The objective of the present work is to get some additional information on the effects of solvent and viscosity on the cage reactions of *tert*-butoxy radicals, in connection with the oxidation of polyolefins where a profound viscosity effect is observed.[12] The viscosity can be varied either by changing the solvent or temperature. In this work, it was varied by using various solvents and their mixtures at constant temperature so as to avoid a possible complication induced by different temperature, such as the effect of temperature on the initial separation of the radical pair.[5] Viscosity spans the range from 0.310 to 4041 cP at 45°. DBPO was used as a source of *tert*-butoxy radicals.

Results and Discussion

DBPO was first decomposed in the presence of radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BMP) in order to ascertain that di-*tert*-butyl peroxide was a cage product under the reaction conditions employed. The results shown in Table I indicate that a small amount of BMP can scavenge substantially all free *tert*-butoxy radical and suppress acetone formation,[13] whereas a high concentration of BMP cannot decrease the formation of di-*tert*-butyl peroxide. These results support that di-*tert*-butyl peroxide is a cage product and is not formed by the bimolecular interaction of free *tert*-butoxy radicals.[14] Thus, the decomposition prod-

(9) R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970).

(10) (a) W. Braun, L. Rajenbach, and F. Eirich, *J. Phys. Chem.*, **66**, 1591 (1961); (b) T. Koenig, *J. Amer. Chem. Soc.*, **91**, 2558 (1969).

(11) (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (1967); (b) *ibid.*, **92**, 5403 (1970); (c) W. A. Pryor, K. Smith, J. T. Echols, Jr., and D. L. Fuller, *J. Org. Chem.*, **37**, 1753 (1972); (d) W. A. Pryor, E. H. Morkved, and H. T. Bickley, *ibid.*, **37**, 1999 (1972).

(12) E. Niki, C. Decker, and F. R. Mayo, *J. Polym. Sci., Part A-1*, **11**, 2813 (1973).

(13) *tert*-Butoxy radical undergoes negligible amounts of β scission or disproportionation in the cage.[11d]

(14) Hiatt and Traylor[7] also found that excess diphenylpicrylhydrazyl

Table I. Effect of Radical Scavenger in the Decomposition of DBPO at 45°, [DBPO] = 0.10 M

Medium	Viscosity,[a] cP	[BMP], M	Products, % of t-BuO—		
			t-Bu$_2$O$_2$	Me$_2$CO	t-BuOH
Benzene	0.473	0	4.5	40.0	43.8
Benzene	0.473	0.050	5.4	2.4	82.9
Benzene + liquid paraffin	3.07	0	20.3	0	78.5
Benzene + liquid paraffin	3.07	0.333	21.9	0	76.6

[a] Measured at 45°.

ucts from DBPO were analyzed and di-*tert*-butyl peroxide was taken as a measure for the extent of cage reaction and p = [di-*tert*-butyl peroxide]/[DBPO] was defined as the probability of geminate recombination.

Some pertinent results that show the effects of viscosity of the medium on the formation of di-*tert*-butyl peroxide are illustrated in Figure 1. The solid circles indicate the system containing polymeric compounds with molecular weight higher than 2000 in the solution. It can be seen that the solutions can be roughly divided into two groups, one with dissolved high molecular weight compound and the other without. In the former solutions, the yield of cage product is rather insensitive to the viscosity, whereas in the latter solutions it increases with increasing viscosity of the media.

Table II summarizes the yield of di-*tert*-butyl per-

Table II. Cage Recombination of *tert*-Butoxy Radicals in Various Neat Solvents at 45°

Solvent	η, cP	t-Bu$_2$O$_2$, %
Silicone oil KF-54	188.0	59.0
Liquid paraffin	47.5	47.3
Di-2-ethylhexyl phthalate	21.3	43.8
Dimethyl phthalate	6.18	28.0
Hexadecane	2.09	22.8
Propylene glycol	15.90	21.5
Dodecane	1.01	12.7
Tetralin	1.61	11.4
Decane	0.670	10.8
o-Dichlorobenzene	1.00	10.3
tert-Butyl alcohol	1.78	9.8
Acetophenone	1.24	8.7
Cumene	0.598	6.8
α-Methylstyrene	0.685	6.5
Ethylbenzene	0.528	6.2
Cyclohexene	0.505	5.8
Toluene	0.472	4.9
Acetic acid	0.865	4.7
Benzene	0.473	4.5
1-Octene	0.393	4.4
Acetonitrile	0.310	2.1
2-Butanol	1.56	Trace
Isopropyl alcohol	1.20	Trace
Ethanol	0.800	Trace
Methanol	0.447	Trace

oxide formed in the decomposition of DBPO in various neat solvents. According to Noyes' approach,[3] the probability of recombination of two radicals initially formed at distance a is represented by

$$1/p = (aA/2b\alpha)(T^{1/2}/\eta) + (a/2b) \tag{1}$$

and cumyl hydroperoxide did not alter the formation of di-*tert*-butyl peroxide and concluded that di-*tert*-butyl peroxide was a cage product.
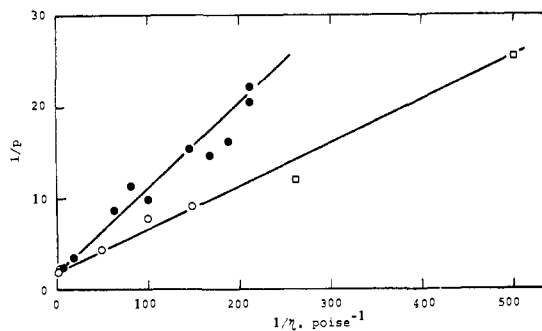
Figure 2. Plots of $1/p$ against $1/\eta$ for the decompositions of DBPO in several neat solvents at 45°: (●) aromatic solvent, (○) aliphatic solvent, (□) aliphatic solvent (data from ref 8).

Figure 3. Plots of $1/p$ against $1/\eta$ for liquid paraffin–benzene (●) and liquid paraffin–isooctane solutions (■).

where A is equal to $(mk/24)^{1/2}/\pi b^2$, constant independent of the nature of solvent, and b, α, T, η, and m denote radius of the radical (assumed to be a sphere), probability of combination on each collision, absolute temperature, viscosity, and mass of the radical, respectively. Equation 1 indicates that at constant temperature the plot of $1/p$ as a function of $1/\eta$ gives a straight line with a slope of $(aA/2b\alpha)T^{1/2}$ and an intercept of $a/2b$. Figure 2 shows some plots for the decompositions of DBPO in various neat solvents at 45°. All the experimental points do not lie on a single straight line, but for solvents of similar properties a fairly good straight line can be obtained. Figure 3 shows the plot of $1/p$ against $1/\eta$ in the mixtures of liquid paraffin and benzene. The data of Kiefer and Traylor[8] obtained also at 45° in liquid paraffin–isooctane solutions are also included in Figure 3.[15] Figure 4 shows the same plot for di-2-ethylhexylphthalate–benzene solutions. All these three plots gave fairly satisfactory straight lines.

Table III summarizes the slopes, intercepts, and

Figure 4. A plot of $1/p$ against $1/\eta$ for 2-ethylhexylphthalate–benzene solutions.

Table III. Slopes, Intercepts, and Calculated α

Radical	Solvent	$aA/2b\alpha$ $\times 10^3$ $P/\deg^{1/2}$	$a/2b$	$\alpha \times 10^2$
$(CH_3)_3CO\cdot$	Di-2-ethylhexyl-phthalate–benzene	6.24	2.0	0.31
$(CH_3)_3CO\cdot$	Liquid paraffin–benzene	5.73	2.0	0.35
$(CH_3)_3CO\cdot$	Neat aromatics	5.06	2.0	0.40
$(CH_3)_3CO\cdot$	Neat aliphatics	2.64	2.0	0.76
$(CH_3)_3CO\cdot$ [a]	Liquid paraffin–isooctane	2.19	2.0	0.92
$(CH_3)_3CO\cdot$, $C_6H_5C(CH_3)_2\cdot$ [b]		0.575	1.23	2.1
$CF_3\cdot$ [c]		0.5	1.1	2–3
$CH_3\cdot$ [d]		0.07	1.1	10–20

[a] Data from ref 8. [b] Reference 6. [c] Reference 4. [d] Reference 5.

probability of combination on each collision, α, calculated assuming A as 10^{-5}. The same intercept for tert-butoxy radical in each medium suggests that the distance between the two tert-butoxy radicals initially formed is independent of the solvent. On the other hand, slopes varied with solvent. Aromatic solvents yield approximately twice as large slopes as aliphatic solvents. Since $a/2b$ is constant independent of solvent,

(15) Viscosities are those determined by Kiefer and Traylor[8] corrected later by Traylor, Table IV in ref 9.
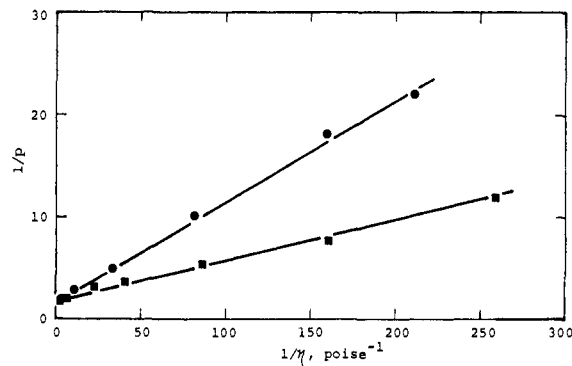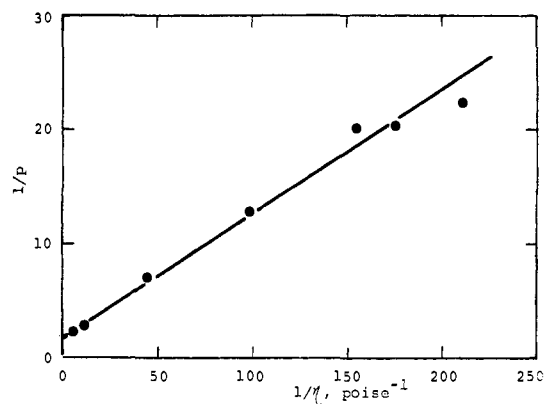
different slopes must be ascribed to different α. In addition, Table II shows that olefins, alcohols, and polar solvents such as acetic acid and acetonitrile gave less cage product than predicted from the corresponding hydrocarbons. These results must imply a specific interaction of caged tert-butoxy radical with surrounding solvent molecules. If tert-butoxy radical forms, for example, π complex, hydrogen bonding, or charge transfer complex with solvents, the probability of recombination should be smaller and these solvents should give lower α and higher slope. This is because the complexing of tert-butoxy radical in the ground state must result in the placing of the solvent molecule in the vicinity of the oxygen and it should desolvate sterically before combining each other to yield di-tert-butyl peroxide. It may be worth pointing out that similar interaction was suggested in the study of solvent effects on the competition between β scission and hydrogen atom abstraction by tert-butoxy radical.[16] Walling and Wagner[16c] found that olefinic and polar solvents such as acetic acid and acetonitrile accelerated the β scission while the hydrogen atom abstraction was relatively solvent insensitive. This also supports the above interpretation that the caged tert-butoxy radical has interaction with the surrounding solvent. Tables I and II indicate that the extent of interaction increases in the order of aliphatic, olefinic, aromatic, and polar compounds such as acetic acid, acetonitrile, and alcohols.

(16) (a) G. A. Russell, J. Org. Chem., 24, 300 (1959); (b) E. L. Patmore and R. J. Gritter, ibid., 27, 4196 (1962); (c) C. Walling and P. Wagner, J. Amer. Chem. Soc., 86, 3368 (1964).

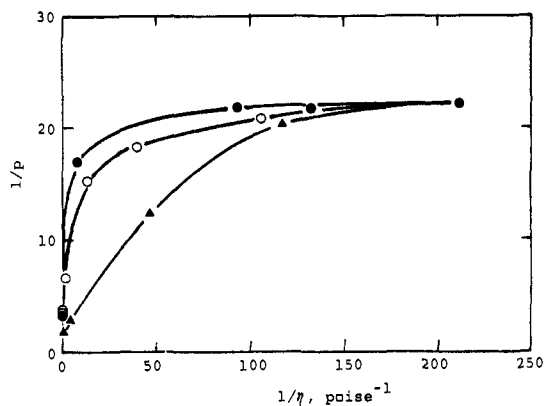Figure 5. Plots of $1/p$ against $1/\eta$ for silicone oil–benzene solutions: (▲) SOKF54, (○) SOKF96, (●) SOKF96H.
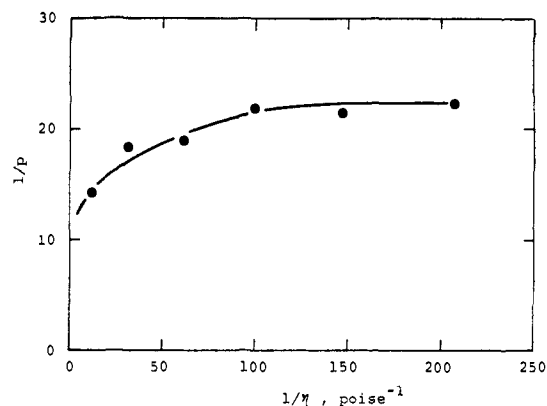

Figure 6. A plot of $1/p$ against $1/\eta$ for polypropylene–benzene solutions.

It is interesting that the formation of the cage product is almost completely suppressed in methanol, ethanol, isopropyl alcohol, and 2-butanol.[17] We assume that this stems from the hydrogen bonding between tert-butoxy radical and alcoholic solvents. It may be worth noting that the autoxidations of methylphenylcarbinol, isopropyl alcohol, and 1,4-cyclohexadiene are retarded markedly by the addition of methanol but not by tert-butyl alcohol.[18]

Table III shows that the probability of combination of tert-butoxy radicals per each collision is considerably smaller than those for tert-butoxy and cumyl radicals and for trifluoromethyl radicals. This must be due to the more restricted orientation of the tert-butoxy radicals necessary for the successful combination.[19] Szwarc and his coworkers[4,5] found that the probability was greater by a factor of 3 to 5 for methyl than for trifluoromethyl radicals, which they interpreted as an indication of faster rotation of methyl radical when compared with trifluoromethyl radical. That the probability for methyl and trifluoromethyl radicals is virtually independent of solvent in contrast to tert-butoxy radicals must be because the former two radicals have much less interaction with solvents than the tert-butoxy radical.

The intercept, $a/2b$, for DBPO is about twice as large as those for tert-butylperoxy-α-phenylisobutyrate, perfluoroazomethane, and azomethane. Kodama[20] has also obtained $a/2b$ which is slightly larger than unity for azomethane. This difference must arise from the type and number of intervening molecules.

Figure 1 shows that when DBPO is decomposed in the solutions containing polymers the probability of geminate recombination is small and relatively insensitive to the viscosity of the bulk solution. For example, although the viscosity of benzene solution containing 0.122 g/ml polystyrene of 498,000 molecular weight is as high as 294.0 cP at 45° compared with 0.493 cP of neat benzene, only 4.6% of the di-tert-butyl

peroxide was formed, which is substantially the same as in neat benzene. That the extent of cage reaction is smaller than expected in the polymer solutions has been observed previously.[21] For example, Guk and Tsepalov[22] found that the efficiency of radical production from azobisisobutyronitrile (AIBN) remained unaltered up to 20 vol % polystyrene in chlorobenzene.[23] In spite of several experimental findings, no systematic study aimed specifically at elucidating the role of high polymers and molecular weight in the cage recombination reaction has yet been carried out.

In order to obtain more information on the characteristic behavior of polymer solutions, DBPO was decomposed in various polymer solutions. DBPO is a suitable radical source since it gives only one cage product which can be easily analyzed. Figure 5 shows the plot of $1/p$ as a function of $1/\eta$ for silicone oil–benzene solutions. A similar plot obtained in the decomposition of DBPO in polypropylene–benzene solutions is shown in Figure 6. Figure 5 indicates that the higher the molecular weight of the polymer dissolved in solution the larger the curvature, that is, the lower the extent of cage reaction at constant viscosity.[24] In order to examine the effect of molecular weight of the polymer, solutions of polystyrenes with narrow molecular weight distribution (weight average molecular weight per number average molecular weight $\leq$ 1.2) were studied. The results in Figure 7 show considerable scatter,[25] but it clearly shows that the higher the molecular weight the lower the yield of cage product at constant viscosity.

The reason for these peculiar phenomena is still obscure and quantitative discussion is difficult at this stage, but a possible explanation for the effect of high molecular weight molecules follows. The macroscopic

(17) A. P. Stefani, G. F. Thrower, and C. F. Jordan, J. Phys. Chem., 73, 1257 (1969), argued that the fraction of cage reactions should be larger in the alcohols since alcohols were "structured" liquids and the average lifetime of a cavity or a cage was likely to be relatively longer than in more normal liquids.

(18) Unpublished work from our laboratory.

(19) L. Batt and S. W. Benson, J. Chem. Phys., 36, 895 (1962), have deduced a rather low value for the rate constant for recombination of tert-butoxy radicals in the gas phase. This is interpreted as being due to an unfavorable entropy term.

(20) S. Kodama, Bull. Chem. Soc. Jap., 35, 824, 827 (1962).

(21) A. M. North, Quart. Rev. Chem. Soc., 20, 421 (1966).

(22) A. F. Guk and V. F. Tsepalov, Kinet. Katal., 12, 910 (1971).

(23) G. Valiquette and N. A. Weir, Chem. Commun., 1071 (1972), recently reported that the extent of cage recombination of 2-cyano-2-propyl radicals from AIBN was dependent on the viscosity of polystyrene–benzene solutions and eq 1 held. However, the viscosity range studied is relatively small (0.8–1.8 cP) and only tetramethylsuccinyldinitrile, one of the four possible cage products, was analyzed.

(24) It is not surprising that eq 1 does not hold for the system containing polymers since in Noyes' model the solvent is treated as continuum, which may not be applicable to polymer solutions. However, the data were treated as in Figures 5, 6, and 7 so as to compare directly with the system where no polymers were involved.

(25) A small error in the yield of di-tert-butyl peroxide gives a large error in $1/p$ when p is small; e.g., an absolute error of 0.5% gives 20% error in $1/p$ when $p = 0.05$.

viscosity of solutions of long-chain molecules contains a contribution from chain tangling effects and it has been argued that the macroscopic viscosity is no measure of the resistance to the translational motion of small solute molecules.[11b,21] For example, Rothschild[26] found that when the viscosity of a solution of methylene chloride–polystyrene was increased as much as several orders of magnitude, the solvent mobility was decreased only by a factor of about 1.2. Benzene is a good solvent for polymers used in this study and polymers are expected to extend their chains and have coiled configurations. The mean radius of the polymer coil will be decreased with an increase in concentration of polymers. When polymers are dissolved in benzene, the macroscopic viscosity increases drastically although the total polymer molecule volume fraction may not increase as much. Therefore benzene must contribute much in forming a cage and the tert-butoxy radicals must have almost as much chance to diffuse out of the cage as in neat benzene except when the polymer concentration is extremely high and the cage is exclusively composed of polymer molecules. Probably, the volume fraction of benzene may be a more important factor governing the extent of cage reaction than the macroscopic viscosity of the polymer solutions. This may be why as high as 80% of the tert-butoxy radicals from DBPO recombined in a bulk atactic polypropylene but only a small amount of solvent was quite effective in reducing the cage recombination.[12]

Experimental Section

Materials. DBPO was prepared by the method of Bartlett, et al.[27] Standard polystyrenes with narrow molecular weight distribution were purchased from Pressure Chemical Co. The physical properties of polystyrenes are summarized in Table IV. Poly-

Table IV. Monodisperse Polystyrene Standard

Mol wt	$[\eta]^a$	M_w/M_n
2,100	0.031	1.10
4,000	0.046	1.10
10,000	0.095	1.06
20,400	0.14	1.06
200,000	0.65	1.06
498,000	1.50	1.20

^{a} Measured at 45° in benzene.

propylene was purified as described elsewhere.[28] Three samples of dimethylpolysiloxanes, SOKF54, SOKF96, and SOKF96H, were kindly supplied from Shinetsu Chemical Ind. The viscosity and molecular weight calculated by the following equation[29] are

$$\log \nu \text{ (cSt)} = 1.00 + 0.0123 M^{0.5} \tag{2}$$

(26) W. G. Rothschild, *Macromolecules*, **5**, 37 (1972).
(27) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).
(28) E. Niki and Y. Kamiya, *J. Org. Chem.*, **38**, 1403 (1973).
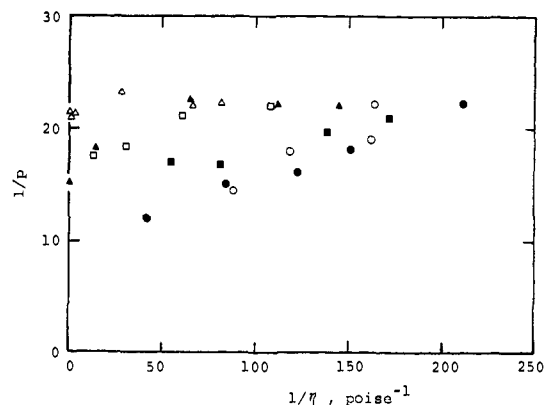(29) A. J. Barry, *J. Appl. Phys.*, **17**, 1020 (1946).

Figure 7. Plots of $1/p$ against $1/\eta$ for polystyrene–benzene solutions. Molecular weights of polystyrenes are (●) 2,100, (O) 4,000, (■) 10,000, (□) 20,400, (▲) 200,000, (△) 498,000.

Table V. Viscosity and Calculated Molecular Weight of Silicone Oils

Sample	Viscosity,^{a} P	Mol wt^b
SOKF54	1.88	10,300
SOKF96	2.36	12,700
SOKF96H	40.71	45,500

^{a} Determined at 45°. ^{b} Calculated from eq 2.

shown in Table V. These oils are assumed to have wide molecular weight distribution. Commercial 2,6-di-tert-butyl-4-methylphenol was recrystallized from methanol. Organic solvents were commercial materials, purified if necessary by conventional method.

Procedures. Dried DBPO (about 0.1 M) and 0.5 ml of appropriate solution were weighed into a 10-mm o.d. ampoule, which was degassed and sealed under vacuum (10^{-6} Torr). The ampoule was immersed into a water bath maintained at 45° and DBPO was allowed to decompose completely in about its 10 half-lives. The half-life of DBPO at 45° was measured in various media including viscous polymer solutions by following the rate of carbon dioxide evolution using a Toepler pump and was obtained as 41 min, in good agreement with the previously reported values of 42 min[27] in benzene and 43.5 min[12] in bulk polypropylene.[30] After the decomposition, the ampoule was opened, internal standard was added by syringe, and the mixture was analyzed with glc equipped with digital integrator using a 3 mm × 7 m Carbowax 20M column. The temperature of the injection port and the column was kept below 90° to avoid the thermal decomposition of di-tert-butyl peroxide in glc. When the reaction mixture was too viscous to syringe directly, the ampoule was connected to the vacuum line and the volatile compounds were transferred first below 0° and finally at 50° under vacuum into a trap cooled with liquid nitrogen. The products from DBPO were di-tert-butyl peroxide, acetone, and tert-butyl alcohol with a small amount of isobutylene oxide. In most of the solutions the material balance was quantitative, although only about 90% of the tert-butoxy group could be accounted for in neat benzene and in very viscous benzene solutions of polystyrene.[28] More than one run was performed in most of the solutions and the average was taken. Viscosities were measured for each solution at 45° using calibrated modified Ostwald viscosimeters.

(30) These results suggest that DBPO is a multibond initiator.