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Interaction between Radicals Derived from Two Di-*t*-Alkyl Peroxides with Some Monomers and Polymers

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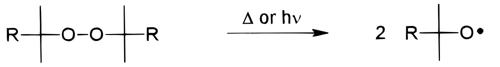
ABSTRACT: The thermolysis of di-*tert*-butyl and di-*t*-amyl peroxides in *n*-decane and with poly(methyl methacrylate) and poly(ethylene glycol) in chlorobenzene has been studied in the presence of tri-*tert*-butylnitrosobenzene as a spin trap. The major reaction pathways of the resulting *t*-alkoxyl radicals were β-scission and hydrogen atom abstraction. Thermolysis of the same peroxides in the presence of methyl methacrylate and methyl acrylate led to the trapping of growing polymer chains alongside unreacted alkyl radicals (again formed via β-scission of the first generation *t*-alkoxyl radicals). In some of the spectra, hyperfine coupling to γ-protons was observed. The hydrogen abstracting ability of radicals present during thermolysis of both peroxides has been compared in the presence of MA.

Introduction

Organic peroxides readily decompose, both thermally and photolytically, because of the weakness of the oxygen−oxygen bond, and consequently, they play an important role as initiators in the radical synthesis of speciality polymers. A common thermal and photochemical initiator is di-*tert*-butyl peroxide, which decomposes to form both the *t*-butoxyl radical (eq 1, R = Me) and



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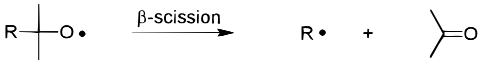
the methyl radical via β-scission (eq 2, R = Me). The



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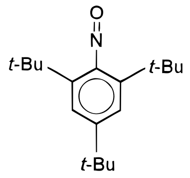
t-butoxyl radical is a good hydrogen atom abstractor which can lead to branching via hydrogen atom abstraction from a growing polymer chain.

On the other hand, di-*t*-amyl peroxide (eqs 1 and 2, R = Et) is still an efficient initiator, yielding the *t*-amyloxyl and ethyl radicals (via β-scission). However, the rate of β-scission of the *t*-amyloxyl radical is at least 1 order of magnitude faster than that of the *t*-butoxyl radical[1,2] leaving the ethyl radical, which is a poor hydrogen atom abstractor, as a more significant initiating species. Consequently, di-*t*-amyl peroxide is often employed under circumstances where control over molecular weights and narrow molecular weight distributions is required.

Clearly, the addition and abstraction reactions of initiating radicals with mono- and polymers is of great importance in polymer chemistry. For example, for *t*-butoxyl radicals, the ratio of hydrogen atom abstraction to addition for methyl methacrylate can be as high as 1:2,[3] leading to a significant proportion of unsaturated end groups in the polymer.

Unfortunately, all of these radicals usually have low steady-state concentrations under typical reaction conditions, and so it is not possible to observe them directly. However, radical trapping techniques can provide the required information. We have employed the spin trapping technique as a simple and expedient means of stabilizing short-lived radicals for electron spin resonance (ESR) study.[1,4] The well-resolved ESR spectra of the resulting spin adducts enables the identification of the radicals present in the system.

We previously have employed 2,4,6-tri-*tert*-butylnitrosobenzene [TTBNB (**1**), sometimes also referred to as BNB; see Structure 1] as a spin trap to preferentially trap carbon-centered radicals which are our main interest in this study.[1] If the trapped radical is bulky, this spin trap can also give anilino adducts by attack at the oxygen atom of the nitroso group. The proportion of the anilino to nitroxyl adduct progresses as follows: $\bullet CH_3$ (almost entirely nitroxyl) < $\bullet CH_2R$ (mixture) < $\bullet CHR_2$ (mixture) < $\bullet CR_3$ (almost entirely anilino).



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In this paper, we describe the results of our research into the interaction of *t*-alkoxyl and alkyl radicals with two low-molecular-weight polymers, poly(methyl methacrylate) (PMMA) and poly(ethylene glycol) (PEG), and with two monomers, methyl methacrylate (MMA) and methyl acrylate (MA).

Experimental Section

Materials. Di-*tert*-butyl peroxide (>99.5% purity, as checked by NMR) and di-*t*-amyl peroxide (>99.5% purity, as checked by NMR) were used as supplied by Elf-Atochem GmbH. PMMA (FW ca. 15 000, Aldrich) was precipitated from hexane before use. PEG 500 (NH_2 end groups, Fluka), MMA, and MA (both Aldrich) were all used as supplied. (Low-molecular-weight samples of the polymers were selected to aid their solubility under our reaction conditions.) All other chemicals, solvents, and spin traps were obtained from Aldrich except PBN-d_{14}, which was obtained from the OMRF spin trap source.

Preparation of Solutions. The concentration of the spin traps was usually in the range 0.04−0.15 mol L^{-1}, and the peroxides were in the range 0.090−0.25 mol L^{-1}. Before thermolysis, all solutions were degassed with nitrogen, for

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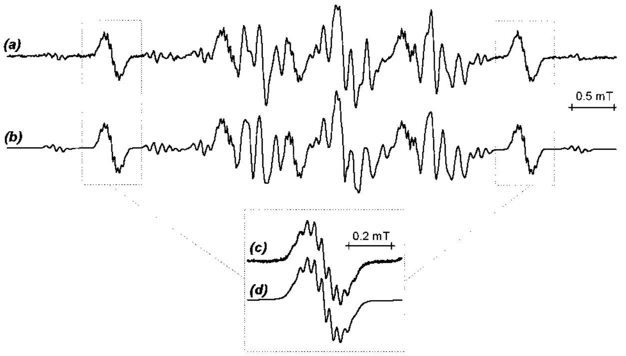


Figure 1. (a) ESR spectrum, recorded after 10 min thermolysis, of di-*tert*-butyl peroxide in *n*-decane at 391 K in the presence of TTBNB. (b) Computer simulation based on the TTBNB nitroxyl adducts of Me• (2%), •CHR_2 (23%), and •CH_2R (3%) and the anilino adducts of •CHR_2 (41%) and •CH_2R (31%), with hyperfine parameters as given in Table 1. (c) An enlarged section of the extreme high- and low-field packet of lines (separately recorded) of the •CHR_2 nitroxyl adduct along with (d) its computer simulation.

between 5 and 10 min, and the sample tube was then tightly sealed. All samples for ESR study were prepared in 4 mm i.d. quartz tubes.

Spectroscopic Measurements. All spectra were recorded on a Bruker EMX X-band spectrometer operating with 100 kHz magnetic field modulation. Thermolysis was undertaken employing the Bruker B-VT1000 variable temperature control system (accurate to ±1 K). Spectra were recorded with a modulation amplitude in the range 0.01−0.02 mT with spectrum accumulation over 4−16 scans.

Thermolysis was undertaken for a period of up to 60 min (varying with the peroxide and the reaction temperature), and spectra were recorded, as required, at various times during this period. Improvements in spectral resolution were sometimes obtained if the solution was further degassed with nitrogen before measurement.

Spectrum simulations were undertaken employing *PEST WinSim*[5] (a NIEHS Public EPR software tool). The percentage contribution of each adduct to the total integrated spectrum area has been calculated for each simulation. The hyperfine splitting constants obtained from these spectral simulations are considered accurate to ±0.005 mT.

Results and Discussion

Thermolysis in the Presence of *n*-Decane. We undertook the thermolysis of di-*tert*-butyl peroxide (0.20 mol L^{-1}) in *n*-decane, as a model for a simple polyethylene oligomer, in the presence of TTBNB (0.05 mol L^{-1}) at 391 K. Di-*tert*-butyl peroxide was selected for this experiment, rather than di-*t*-amyl peroxide, as the radicals present during its thermolysis are more aggressive hydrogen atom abstractors,[1] thus maximizing the possibility of trapping *n*-decane-derived radicals.

The resulting ESR spectrum consisted of a mixture of five different adducts (Figure 1a). One of these (2%) is the nitroxyl adduct of the Me• radical formed, as always, via β-scission of the *t*-butoxyl radical.[1] The major adducts (64% of the total integrated spectrum area) are the nitroxyl (23%) and anilino (41%) forms of a secondary carbon-centered radical that can be assigned to the adducts of radicals formed by hydrogen atom abstraction from one of the CH_2 groups. The nitroxyl adduct is particularly interesting with hyperfine coupling to 4 equivalent γ-hydrogen atoms clearly observed (Figure 1c). Resolved hyperfine coupling to γ-hydrogen atoms is observed only rarely in TTBNB adducts,[6,7] probably because of line broadening resulting from a large number of unresolved hyperfine interactions.

The remaining two adducts, which account for the remaining 34% of the total integrated spectrum area, are the nitroxyl (3%) and anilino (31%) adducts derived from a primary carbon-centered radical. We assign these adducts to the trapping of radicals formed via abstraction of a methyl hydrogen atom. The parameters for all of the adducts are summarized in Table 1.

These results indicate that the *t*-butoxyl radical, and possibly the methyl radical, would be expected to readily abstract hydrogen atoms from a polymer chain and the methyl groups along that chain.

Thermolysis in the Presence of PEG. Thermolysis of di-*tert*-butyl peroxide (0.20 mol L^{-1}) in the presence of PEG 500 and TTBNB (0.04 mol L^{-1}) was undertaken in a 50:50 (v/v) PEG/chlorobenzene solution at 373 K and resulted in the formation of a single spin adduct. This is an anilino adduct derived from a secondary carbon-centered radical that can be assigned to the radical formed by hydrogen atom abstraction from the CH_2 groups along the polymer chain. There is no evidence for any nitroxyl methyl radical adducts, indicating that abstraction from the polymer chain by the *t*-butoxyl radical is relatively fast and efficient compared to β-scission.

When the experiment was repeated with di-*t*-amyl peroxide, with the peroxide concentration adjusted (to 0.090 mol L^{-1}) to give as nearly as possible the same radical input into the system per second, the ESR spectrum consisted of a mixture of three adducts. The major species were the nitroxyl (40%) and anilino (21%) adducts of the ethyl radical. The remaining adduct arises from the same •CHR_2 anilino adduct as observed employing di-*tert*-butyl peroxide but with a reduced

Table 1. Hyperfine Splitting Constants (in mT) for the ESR Spectra of the Various TTBNB Spin Adducts of Radicals Formed during the Thermolysis of Di-*t*-alkyl Peroxides in the Presence of Decane, PEG, and PMMA

radical	solvent	T/K	adduct	a(N)	$a(H_\beta)$	$a(H\gamma)$	a(2m-H)
$-CH_2C(\bullet)HCH_2-$	decane	391	nitroxyl[a]	1.345	2.104 (1H)	0.040 (4H)	0.074
	decane	391	anilino[a]	1.063	0.124 (1H)		0.185
$\bullet CH_2(CH_2)_8CH_3$	decane	391	nitroxyl[a]	1.340	1.700 (2H)		0.080
	decane	391	anilino[a]	1.034	0.233 (2H)		0.175
$\bullet CH_3$	decane	391	nitroxyl[a]	1.330	1.100 (3H)		0.090
	chlorobenzene	382	nitroxyl[a]	1.309	1.226 (3H)		0.085
$-OC(\bullet)HCH_2-$	chlorobenzene	373	anilino[a,b]	1.051	0.070 (1H)		0.184
$\bullet CH_2CH_3$	chlorobenzene	382	nitroxyl[b]	1.354	1.722 (2H)		0.083
	chlorobenzene	382	anilino[b]	1.191	0.232 (2H)		0.178
$-CH(\bullet)C(Me)(CO_2Me)-$	chlorobenzene	382	anilino[a,b]	1.000	0.050 (1H)		0.191
$-CH_2C(CH_2\bullet)(CO_2Me)-$	chlorobenzene	382	nitroxyl[a]	1.355	1.728 (2H)		0.071
	chlorobenzene	382	anilino[a]	1.173	0.214 (2H)		0.143

[a] Employing di-*t*-butyl peroxide. [b] Employing di-*t*-amyl peroxide.

contribution (39%). The parameters of the various adducts are summarized in Table 1.

We believe that these observations are in accord with the different hydrogen atom abstracting abilities of the radicals produced during thermolysis. The concentration of the *t*-alkoxyl radical, which is the radical primarily responsible for hydrogen atom abstraction, is much reduced in the case of di-*t*-amyl peroxide compared to di-*tert*-butyl peroxide because of the much faster β-scission of the *t*-amyloxyl radical.[1,2]

Double integration of the spectra obtained during the thermolysis of both peroxides gives the total relative concentrations of adducts formed in the two experiments. Adjusting these concentrations to allow for a slightly different radical input into the system per second in the two experiments gives the ratio of radicals derived from the polymer by hydrogen atom abstraction during the thermolysis of di-*tert*-butyl peroxide to those derived during the thermolysis of di-*t*-amyl peroxide as ca. 22:1 at 373 K.

Thermolysis in the Presence of PMMA. Thermolysis of di-*tert*-butyl peroxide (0.178 mol L^{-1}) in the presence of PMMA (407 g L^{-1}) and TTBNB (0.04 mol L^{-1}) in chlorobenzene at 382 K results in the formation of four spin adducts. One of these (13%) is the nitroxyl adduct of the Me• radical. The major adduct (75%) is an anilino adduct derived from a secondary carbon-centered radical which can be assigned to the radical formed by hydrogen atom abstraction from the CH_2 groups along the polymer chain. The remaining two adducts are a nitroxyl adduct (2%) and an anilino (10%) adduct derived from a primary carbon-centered radical. We assign these adducts to radicals formed via abstraction of a methyl hydrogen atom from the polymer.

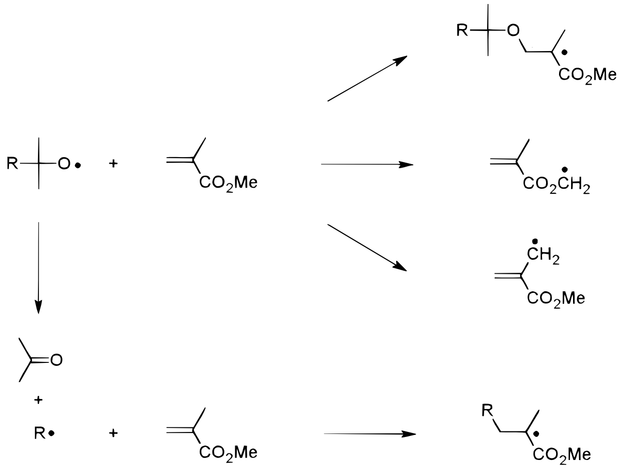
The experiment was repeated with di-*t*-amyl peroxide with the peroxide concentration adjusted (to 0.090 mol L^{-1}) to give, again, as nearly as possible the same radical input into the system per second, with all other parameters remaining unchanged. The ESR spectrum again consisted of a mixture in which the major species are the nitroxyl (46%) and anilino (23%) adducts of the ethyl radical. The remaining contribution arises from the same $\bullet CHR_2$ anilino adduct as observed employing di-*tert*-butyl peroxide but with a reduced contribution (31%). The parameters for all of the adducts are summarized in Table 1.

We would anticipate abstraction from the methyl groups to be less significant when employing di-*t*-amyl peroxide than when employing di-*tert*-butyl peroxide. We did not observe the appropriate adduct although a small percentage could be hidden by the nitroxyl and anilino forms of the ethyl adduct. These observations are, again, in accord with the different hydrogen atom abstracting abilities of the radicals produced during thermolysis.

Double integration of the spectra obtained during the thermolysis of both peroxides, making the same adjustments as described above, gives the ratio of radicals derived from the polymer by hydrogen atom abstraction during the thermolysis of di-*tert*-butyl peroxide to those derived during the thermolysis of di-*t*-amyl peroxide as ca. 5.3:1 at 382 K.

Thermolysis in the Presence of MMA. The thermolysis of di-*tert*-butyl peroxide (0.207 mol L^{-1}) in chlorobenzene in the presence of MMA (0.420 mol L^{-1}) and TTBNB (0.057 mol L^{-1}) was undertaken at 382 K. Because the *t*-butoxyl radical is an efficient hydrogen abstractor, both abstraction from and addition to MMA can be anticipated, whereas the methyl radical, a poorer hydrogen atom abstractor, would be expected to react predominantly with MMA via addition.[8] These reactions are summarized in Scheme 1 (R = Me).

Scheme 1



The ESR spectrum consists of a mixture in which the major species (94%) is an anilino adduct of a tertiary alkyl radical which can be assigned to the trapping of the growing polymer chain.[9] The minor species is the nitroxyl adduct of the methyl radical (formed via β-scission of the *t*-butoxyl radical). No other nitroxyl or anilino adducts are observed.

In neat MMA (ca. 9.25 mol L^{-1}), at 333 K, nitroxyl radical scavenger techniques have shown that hydrogen atom abstraction by the *t*-butoxyl radical from the allylic methyl group forms ca. 29% of the reaction pathway compared to ca. 62% formed via addition to the monomer, with approximately 4.6% of the total products formed via reactions of the methyl radical.[10] However, under the conditions of our experiment ([MMA] = 0.420 mol L^{-1} in chlorobenzene), reaction products derived from the bimolecular reaction of the *t*-butoxyl radical with MMA will be reduced by a factor of ca. 0.045 compared to the unimolecular β-scission reaction. That is, the percentage of products derived from reactions of the *t*-butoxyl radical should be very similar to those derived from the methyl radical. In addition, the proportions of the two radicals could be further affected by the change from neat MMA to chlorobenzene solution and by the change in temperature from 333 to 382 K.

In light of the above discussion, $\bullet CH_2R$ radicals derived via hydrogen atom abstraction from the allylic methyl group might be expected to form a significant reaction product. In neat MMA at 373 K, however, we only observe the same anilino adduct as that observed in chlorobenzene solution, with no evidence for any $\bullet CH_2R$ adducts (or, indeed, for the methyl adduct). TTBNB has proved a successful spin trap for radicals such as methyl, ethyl, and benzyl, plus many other $\bullet CH_2R$ radicals,[1,7] and the absence of $\bullet CH_2R$ adducts from the ESR spectrum could be due to two possibilities. First, such radicals are formed but react with monomer in preference to the spin trap, and second, at our reaction temperature (373 K), their concentration is less than that predicted at 333 K.

The experiment in chlorobenzene was repeated with di-*t*-amyl peroxide with the peroxide concentration adjusted (to 0.095 mol L^{-1}) to give as nearly as possible the same radical input into the system per second, with

Table 2. Hyperfine Splitting Constants (in mT) for the ESR Spectra of Various TTBNB Spin Adducts of Radicals Formed during the Thermolysis of Di-*t*-alkyl Peroxides in the Presence of MMA and MA

radical	solvent	T/K	adduct	a(N)	$a(\mathrm{H}_\beta)$	$a(\mathrm{H}\gamma)$	a(2m-H)
$\bullet\mathrm{CH}_3$	chlorobenzene	382	nitroxyl[a]	1.309	1.221 (3H)		0.081
	toluene	382	nitroxyl[a]	1.303	1.210 (3H)		0.075
$\bullet\mathrm{CH}_2\mathrm{CH}_3$	chlorobenzene	382	nitroxyl[b]	1.354	1.721 (2H)		0.076
	toluene	382	nitroxyl[b]	1.344	1.705 (2H)		0.079
$-\mathrm{CH}_2\mathrm{C}(\bullet)(\mathrm{CO}_2\mathrm{Me})(\mathrm{Me})$	chlorobenzene	382	anilino[a,b]	0.997			0.197
	MMA	373	anilino[a]	0.995			0.199
$-\mathrm{CH}_2\mathrm{C}(\bullet)\mathrm{H}(\mathrm{CO}_2\mathrm{Me})$	chlorobenzene	382	nitroxyl(A)[a]	1.352	2.116 (1H)	0.041 (2H)	0.075
	chlorobenzene	382	nitroxyl(A)[b]	1.352	2.117 (1H)	0.041 (2H)	0.076
	toluene	382	nitroxyl(A)[a,b]	1.352	2.108 (1H)	0.040 (2H)	0.073
	chlorobenzene	382	nitroxyl(B)[a]	1.347	2.074 (1H)	0.030 (2H)	0.079
	chlorobenzene	382	nitroxyl(B)[b]	1.349	2.082 (1H)	0.030 (2H)	0.079
	toluene	382	nitroxyl(B)[a,b]	1.339	2.070 (1H)	0.030 (2H)	0.081
	chlorobenzene	382	anilino[a,b]	0.969	0.211 (1H)		0.164
	toluene	382	anilino[a]	1.055	0.190 (1H)		0.150
$\mathrm{PhCH}_2\bullet$	toluene	382	nitroxyl[a,b]	1.363	1.394 (2H)		0.077
	toluene	382	anilino[a]	1.161	0.220 (2H)		0.170

[a] Employing di-*t*-butyl peroxide. [b] Employing di-*t*-amyl peroxide.

all other parameters remaining unchanged. The ESR spectrum again consisted of a mixture in which the major species (93%) is the same anilino adduct as that observed employing di-*tert*-butyl peroxide. The minor species is the nitroxyl adduct of the ethyl radical. Again, no other nitroxyl or anilino adducts were observed.

Double integration of the spectra obtained from both peroxides in chlorobenzene at 382 K shows that the concentration of the anilino adduct is virtually identical irrespective of which peroxide is employed. Given that the rate of elimination of ethyl from *t*-amyloxyl exceeds that of methyl by a factor of ca. 32−33 at 382 K,[1,11] alkyl radicals will form a much more significant species during the thermolysis of di-*t*-amyl peroxide than during the thermolysis of di-*tert*-butyl peroxide. Hence, the radicals formed from both peroxides initiate approximately the same number of polymer chains irrespective of their nature.

The hyperfine parameters of all of the various adducts are summarized in Table 2.

Thermolysis in the Presence of MA. The results of the experiments in MA support those obtained in the presence of MMA. The thermolysis of di-*tert*-butyl peroxide (0.230 mol L^{-1}) at 382 K in chlorobenzene in the presence of MA (0.381 mol L^{-1}) and TTBNB (0.039 mol L^{-1}) results in an ESR spectrum consisting of a mixture of three adducts (Figure 2a). The major species are a nitroxyl adduct (63%; this spectrum is discussed in more detail below) and an anilino adduct (34%) of a secondary carbon-centered radical. Both of these adducts can be assigned to the trapping of the growing polymer chain. The minor species is the nitroxyl adduct of the methyl radical (3%). No other nitroxyl or anilino adducts, such as those which might be formed following hydrogen atom abstraction from the methyl group of MA, are observed.

The experiment was repeated with di-*t*-amyl peroxide with the peroxide concentration adjusted (to 0.110 mol L^{-1}) to give as nearly as possible the same radical input into the system per second, with all other parameters remaining unchanged. The ESR spectrum (Figure 2e) again consisted of a mixture in which the major species (53%) is the same nitroxyl adduct as observed employing di-*tert*-butyl peroxide. The other major contribution to the spectrum is an anilino adduct (42%) which spectrum simulations indicate is the same anilino adduct as that observed employing di-*tert*-butyl peroxide. The minor species is the nitroxyl adduct of the ethyl radical (5%). It is possible that a small percentage of the ethyl anilino adduct is present but is hidden by the other adducts.

The ESR parameters of the various adducts reported above are summarized in Table 2.

The secondary carbon nitroxyl adduct of the growing polymer chain observed during the thermolysis of both di-*tert*-butyl and di-*t*-amyl peroxide shows resolved coupling to γ-hydrogen atoms. This is seen most clearly in the outermost high and low field groups of lines of the adduct (Figure 2c,g, respectively)]. However, closer examination of these two groups clearly shows that, unlike the spectrum of the *sec*-decyl nitroxyl adduct discussed above (Figure 1c), the two groups are asymmetric and, in fact, are comprised of a mixture of two adducts.

Detailed spectral simulation of these two groups of lines indicate that the ratio of the two nitroxyl adducts is 2.15:1 when employing di-*tert*-butyl peroxide (Figure 2d) and 2.12:1 when employing di-*t*-amyl peroxide (Figure 2h). That is, their proportions the same, within experimental error, irrespective of which peroxide is employed. This seems to eliminate the possibility that the hyperfine couplings are being perturbed by the end group, i.e., by the addition of either an alkyl or an alkoxyl radical. Quite different proportions of the two end groups would be expected from the two peroxides because of the much faster β-scission associated with the *t*-amyloxyl radical.

It would appear, therefore, that we are observing two isomers of the adduct which interchange slowly on the ESR time-scale. Because of the similarity of the hyperfine couplings in both adducts, the environment of the atoms in the two isomers must be very similar.

Again, double integration of the spectra indicates that approximately the same number of polymer chains have been initiated irrespective of the peroxide employed.

Hydrogen Atom Abstraction Ability of Peroxide-Derived Radicals in the Presence of MA. The hydrogen atom abstracting ability of radicals derived from peroxides are important in grafting reactions in

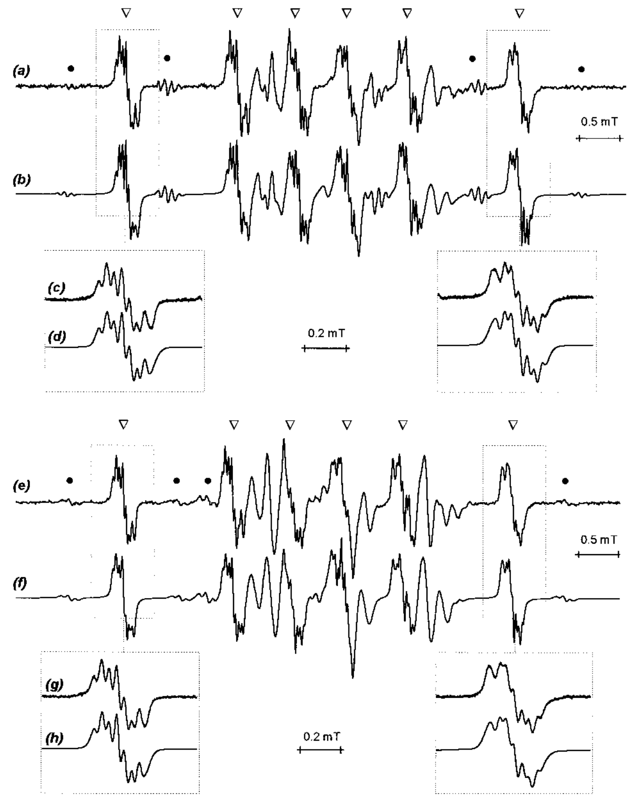
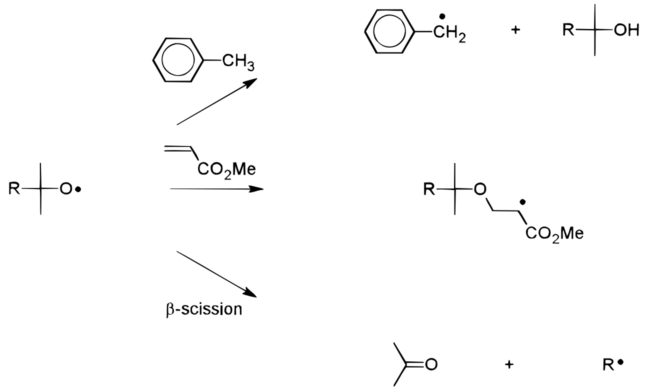


Figure 2. ESR spectrum, recorded after 15 min thermolysis, of (a) di-*tert*-butyl peroxide and (e) di-*t*-amyl peroxide in chlorobenzene at 382 K in the presence of TTBNB and MA. (b) Computer simulation of di-*t*-butyl peroxide based on the TTBNB nitroxyl adducts of Me• (3%, groups of peaks that do not overlap with lines of other adducts are indicated in part a by •), and $-CH_2C(\bullet)H(CO_2Me)$ (63%, main groups of peaks indicated in part a by ▽), and the anilino adduct of $-CH_2C(\bullet)H(CO_2Me)$ (34%) hyperfine parameters (as given in Table 2). (c) Enlarged sections of the extreme high- and low-field packets of lines (separately recorded) of the $-CH_2C(\bullet)H(CO_2Me)$ nitroxyl adduct along with (d) their computer simulations. (f) Computer simulation of di-*t*-amyl peroxide based on the TTBNB nitroxyl adducts of Et• (5%, groups of peaks that do not overlap with lines of other adducts are indicated in part e by •), and $-CH_2C(\bullet)H(CO_2Me)$ (53%, main groups of peaks indicated in part e by ▽), and the anilino adduct of $-CH_2C(\bullet)H(CO_2Me)$ (42%) hyperfine parameters (as given in Table 2). (g) Enlarged sections of the extreme high- and low-field packets of lines (separately recorded) of the $-CH_2C(\bullet)H(CO_2Me)$ nitroxyl adduct along with (h) their computer simulations.

which both monomers and growing polymer chains are present. To gain an insight into the hydrogen atom abstraction ability of the *t*-alkoxyl and alkyl radicals present during the thermolysis of di-*tert*-butyl peroxide and di-*t*-amyl peroxide, we have undertaken the above experiments in toluene, rather than chlorobenzene, thus allowing hydrogen atom abstraction from toluene, in the presence of MA, to compete with addition to monomers and β-scission of the *t*-alkoxyl radical. The essential reactions are shown in Scheme 2.

During the thermolysis of di-*tert*-butyl peroxide (0.252 mol L^{-1}) in the presence of TTBNB (0.055 mol L^{-1}) and MA (0.341 mol L^{-1}) at 382 K the benzyl adduct contributed 38% to the total integrated ESR spectrum area, the adduct of the growing polymer chain contributes 60%, and the methyl radical adduct contributes 2%. When the experiment was repeated at 382 K with di-*t*-amyl peroxide, with the peroxide concentration adjusted to give as nearly as possible the same radical input into the system per second (0.139 mol L^{-1}) ([TTBNB] = 0.055 and [MA] = 0.341 mol L^{-1}), the benzyl nitroxyl adduct contributed 4%, the nitroxyl adduct of the growing polymer chain contributed 85%, and the ethyl nitroxyl radical adduct contributed 11%.

Scheme 2



These results are entirely consistent with the differing lifetimes of the *t*-butoxyl and *t*-amyloxyl radicals (due to different rates of β-scission) and with the greater hydrogen atom abstracting ability of *t*-alkoxyl compared to alkyl radicals. In the experiment with di-*tert*-butyl peroxide, the relatively high concentration of *t*-butoxyl radicals present results in significant hydrogen atom abstraction from toluene. Both *t*-butoxyl radicals and methyl radicals undergo addition to monomers, but in the case of the methyl radical, addition to monomers competes with addition to TTBNB. Consequently, a small percentage of the methyl radical adduct is observed. In the experiment with di-*t*-amyl peroxide, the relatively low concentration of *t*-amyloxyl radicals present results in less hydrogen atom abstraction from toluene. However, because of the higher concentration of alkyl radicals present, a larger percentage of the ethyl radical adduct is observed.

These experiments confirm a significant difference in the hydrogen abstracting ability in the radicals present during the thermolysis of these two peroxides and give an important insight into their application to graft polymerization. Clearly, di-*tert*-butyl peroxide has a greater grafting efficiency than di-*t*-amyl peroxide when employed as an initiator. Our results are in accord with the results of the slightly different experiments of Watanabe et al.[12] who undertook similar experiments employing cyclohexane as a hydrogen atom source and 2,4-diphenyl-4-methyl-1-pentene as a radical trap.

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