Observation of steric effect in radical polymerization of dialkyl fumarates by spin trapping with 2,4,6-tri-tert-butylnitrosobenzene

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Polymer radicals derived from diethyl, diisopropyl, dicyclohexyl and di-tert-butyl fumarates were spin-trapped with 2,4,6-tri-tert-butylnitrosobenzene (BNB), which yields an anilino radical and a nitroxide depending on the steric environment of the radical centre. The spin adduct was prepared by fumarate polymerization initiated with di-tert-butyl hyponitrite in the presence of BNB and by the reaction with active poly(fumarate) radical. According to the e.s.r. spectra of the spin adducts, increases in the bulkiness of the ester alkyl group and the polymer chain length brought about a larger quantity of the anilino radical. This finding indicates the tendency that the reactivity of poly(fumarate) radical toward BNB is differentiated by the steric hindrance caused by the polymer chain and the ester alkyl group.

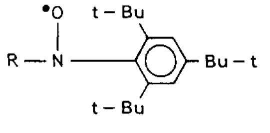
(Keywords: radical polymerization; dialkyl fumarate; steric effect; spin trapping; 2,4,6-tri-tert-butylnitrosobenzene)

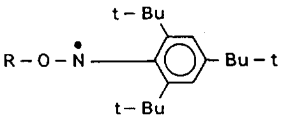
INTRODUCTION

Recently, dialkyl fumarates (DRF) have been noted to yield polymers consisting of a poly(substituted methylene) structure[1–4], despite considerable steric hindrance[5]. Based on the polymerization data of DRF, the role of the bulky ester alkyl group in the facile polymerization to high-molecular-weight polymer has been emphasized[6].

Further studies on DRF polymerization have revealed an extraordinarily high concentration of the polymer radical in the steady state and exceptionally small values for the rate constants of elementary reactions[7,8]. Consequently, the propagating radicals of DRF were detected by e.s.r. spectroscopy at room temperature[7–10]. Spin trapping with 2-methyl-2-nitrosopropane and the spectra of the deuterated fumarates corroborated formation of a substituted methylene radical during DRF polymerization[11].

A space-filling molecular model of poly(DRF) shows that the consecutive carboalkoxymethylene unit causes steric overcrowding along the whole chain, leading to a semi-flexible polymer[6]. Considering the short-lived nature of the 1,2-dicarboethoxy-1-ethyl radical (succinyl radical)[12], a role for the polymer chain in the persistence of poly(DRF) radical can be expected. Spin trapping with 2,4,6-tri-tert-butylnitrosobenzene (BNB) seems to be one of the most promising techniques for revealing the peculiarities in DRF polymerization because BNB affords two types of adducts: a nitroxide (I) or an N-alkoxyanilino radical (II), depending on the steric circumstances of the radical centre[13].


I


II

Primary alkyl radicals have been shown to attack the nitrogen atom of BNB generating the nitroxide, I. Since the tert-butyl groups in the 2- and 6-positions of BNB prevent the attack of the bulky radical on the nitrogen, tertiary alkyl radicals yield solely II. Secondary alkyl radicals tend to react at the nitrogen and oxygen to produce the corresponding spin adducts. Steric congestion around the radical centre results in an increase in the amount of II, and a proportion of II in the spin adduct can be a measure of steric hindrance. The utility of spin trapping with BNB in polymer chemistry has been proved by trapping of propagating radicals from vinyl monomers[14], initiating radicals of a multi-component system[15], radicals generated during degradation of poly(methyl methacrylate)[16], and radicals formed by addition of benzoyloxy radical to styrene and vinyl acetate[17].

In this study, the spin trapping technique employing BNB was applied to clarify the steric environment of the propagating radicals of DRF. The quite slow propagation permitted a reaction with BNB at different stages of propagation. Polymer radicals from alkyl acrylates (RA) structurally akin to poly(DRF) radicals with respect to the radical centre were also submitted to the spin trapping experiment.

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EXPERIMENTAL

Monomers

Diethyl fumarate (DEF) and diisopropyl fumarate (DiPF) were used after distillation under reduced pressure. Di-cyclohexyl fumarate (DcHF) and di-tert-butyl fumarate (DtBF) were supplied by Nippon Oil & Fats Co. Ltd and were used after recrystallization. Ethyl acrylate (EA), isopropyl acrylate (iPA) and tert-butyl acrylate (tBA) were distilled under reduced pressure before use. Cyclohexyl acrylate (cHA) was prepared by the reaction of acryloyl chloride with cyclohexanol and purified by distillation.

Trapping agent

2,4,6-Tri-tert-butylaniline was synthesized by reduction of 2,4,6-tri-tert-butylnitrobenzene, which was prepared by nitration of 1,3,5-tri-tert-butylbenzene[18]. BNB was prepared by oxidation of the aniline and purified as described in the literature[19]: m.p. 172–173°C and $\lambda_{max} = 751$ nm with $\varepsilon = 50$ in benzene (literature values[19], m.p. 167–168°C and $\lambda_{max} = 765$ nm with $\varepsilon = 56.7$ in n-hexane).

Other reagents

1,1′-Azobiscyclohexane-1-carbonitrile (ACN) was recrystallized from methanol. *Trans*-di-tert-butyl hyponitrite (DBH) was prepared and purified according to the method described in the literature[20]; tert-butyl peroxide was distilled under reduced pressure.

Spin trapping

The polymerization mixture consisting of DRF or RA, benzene, DBH and BNB in an e.s.r. tube was sealed off under vacuum and was heated in the cavity of the e.s.r. instrument at 40°C. Alternatively, after the polymerization of DRF sensitized with ACN in one of the arms of an H-shaped ampoule equipped with an e.s.r. tube[11] upon irradiation with a 100 W mercury lamp, a benzene solution of BNB in another arm was added to the polymerization mixture through a stopcock with a Teflon bore. Then, the mixture containing the spin adduct was transferred into the e.s.r. tube under vacuum.

E.s.r. measurement

All the e.s.r. spectra were recorded on a JEOL ME2X spectrometer operated at the X band with a 100 kHz modulation. An e.s.r. tube with a 3 mm outer diameter was used. The e.s.r. spectra were simulated by using a modified program originally reported by Stone and Maki[21].

Consumption rate of BNB

A benzene solution of DRF (1 mol dm^{-3}), DBH (0.01 mol dm^{-3}) and BNB (0.01 mol dm^{-3}) was charged into an ampoule equipped with a cell for visible spectroscopy and sealed off under vacuum. DBH was decomposed in a thermostatically monitored cell in a Shimadzu UV-160 spectrophotometer at 40°C. The concentration of BNB unchanged was calculated from the absorbance at 751 nm.

RESULTS AND DISCUSSION

Spin trapping of poly(DRF) radical initiated with DBH

Figure 1 shows the e.s.r. spectra of poly(DRF) radicals detected during the polymerization. The spectra exhibit complicated hyperfine structure depending on the ester alkyl group. When the polymerization of DRF was initiated with DBH in the presence of BNB (0.01 mol dm^{-3}), only poly(DRF) radical was trapped:

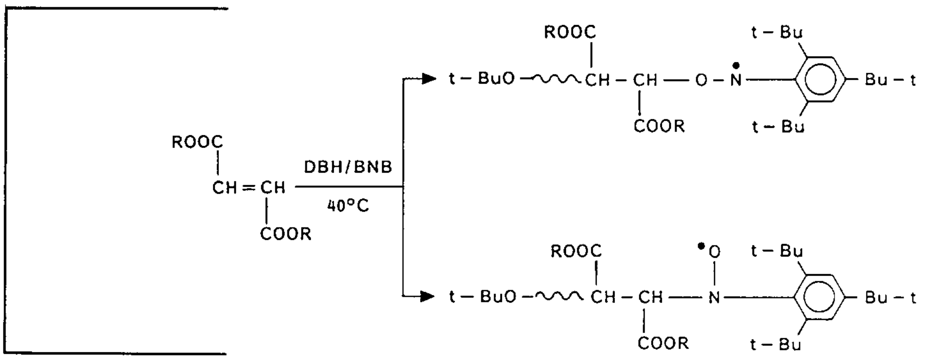


Figure 2 shows the spectrum of the spin adduct from poly(DEF) radical and the computer simulation. The simulated spectrum is almost identical to the observed spectrum. The spectra of the adducts of other poly(DRF) radicals are illustrated in *Figure 3*. The two types of the adducts were readily distinguishable on the basis of the splitting constants and the g values. The spectra of the nitroxides are split by the nitrogen and the α-hydrogens to a triplet of doublet, and the anilino radical is observed as a triplet of triplet as a result of splitting by the nitrogen and m-hydrogens. The e.s.r. parameters evaluated for the nitroxide ($g \simeq 2.0060$) and the anilino radical ($g \simeq 2.0040$) are quite similar to those for the respective adducts of poly(DEF) radical. The composition of the spin adduct is given in *Table 1*.

Poly(DiPF) yielded a larger amount of the anilino radical than poly(DcHF) radical in the presence of 0.01 mol dm^{-3} of BNB, as shown in *Table 1*. Considering differences in DRF concentration, it can be expected that the amount of the anilino radical increases in the order DtBF > DcHF > DiPF > DEF and steric hindrance around the radical centre increases in the same order. However, it should not be hastily concluded that the size of the alkyl group is a main factor in controlling the steric effect, because BNB trapped the polymer radicals at different chain lengths in competition with termination.

To trap poly(DRF) radical at shorter chain lengths, DRF and BNB concentrations were decreased and increased, respectively. As a result, the spectrum of the adduct exhibits an appreciable decrease in the line width and the amount of the anilino radical was also reduced, as shown in *Figure 4*. The steric hindrance was diminished with a decrease in the chain length of poly(DRF) radical.

The splitting constants evaluated from the spectra of

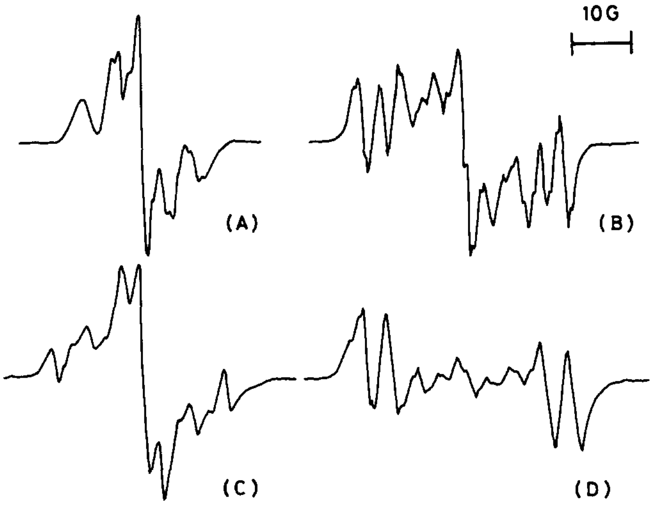


Figure 1 E.s.r. spectra of poly(DRF) radicals observed in polymerizations of DEF (A), DiPF (B), DcHF (C) and DtBF (D) in benzene initiated with di-tert-butyl peroxide under irradiation of a mercury lamp at room temperature

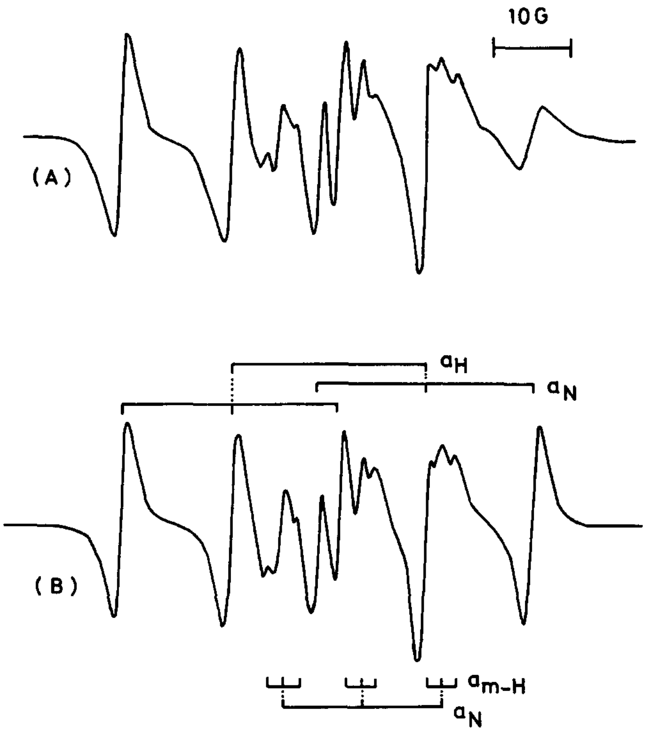


Figure 2 E.s.r. spectrum of spin adduct formed by polymerization of DEF (4.10 mol dm^{-3}) with 0.05 mol dm^{-3} of DBH in the presence of 0.01 mol dm^{-3} of BNB for 60 min at 40°C (A) and computer simulation using $a_N = 13.4$, $a_H = 23.9$ and $a_{m\text{-}H} = 0.8$ G for the nitroxide, and $a_N = 10.2$, $a_{m\text{-}H} = 1.8$ and $a_H = 0.3$ G for the anilino radical (B)

the nitroxide in *Figure 4* ($g = 2.0057$–2.0059) are $a_N = 13.0$–13.2, $a_H = 23.2$–23.8, and $a_{m-H} = 0.8$–1.1 G. Those for the anilino radical ($g = 2.0030$–2.0035) are $a_N = 10.0$–10.2 and $a_{m\text{-}H} = 1.8$–2.2 G, and $a_H < 0.5$ G. The content of the anilino radical in the spin adduct is shown in *Table 1*, indicating that smaller amounts of the anilino radical were produced at 0.1 mol dm^{-3} of BNB. However, poly(DRF) radicals with the bulkier alkyl groups, poly(DcHF) and poly(DtBF) radicals, yielded larger amounts of the anilino radical than those with the smaller alkyl groups, poly(DEF) and poly(DiPF) radicals.

Spin trapping of poly(DRF) radical in H-shaped ampoule

Since the steady-state concentration of the propagating radical has been shown to reach as high as 10^{-5}–10^{-4} mol dm^{-3} (refs 7, 8), BNB was able to trap the

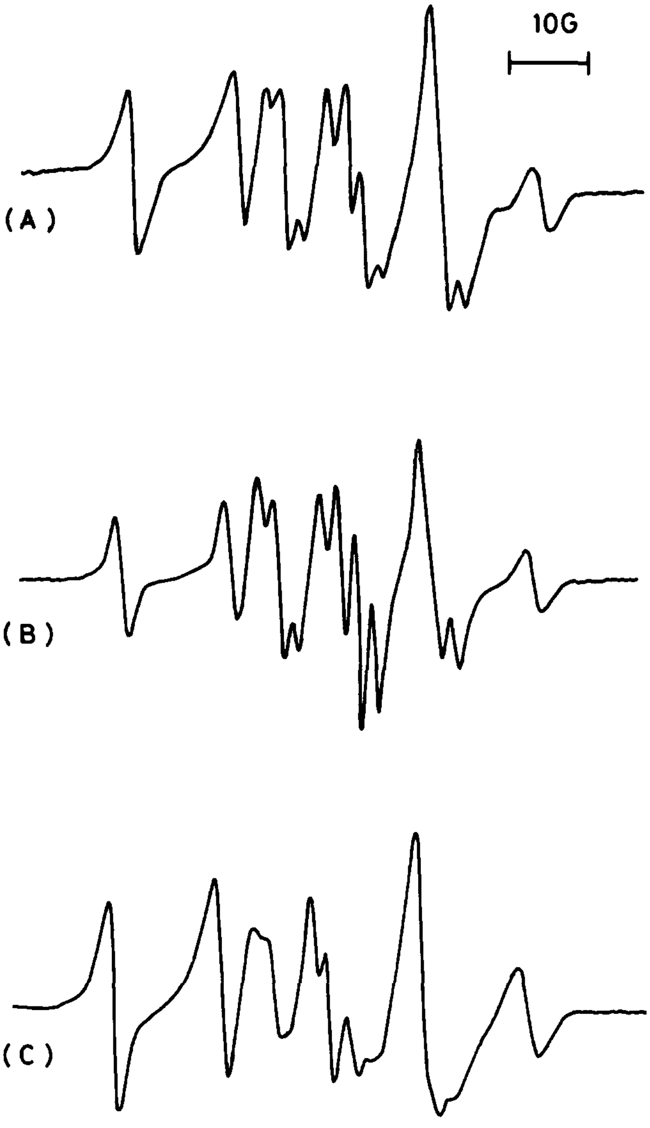
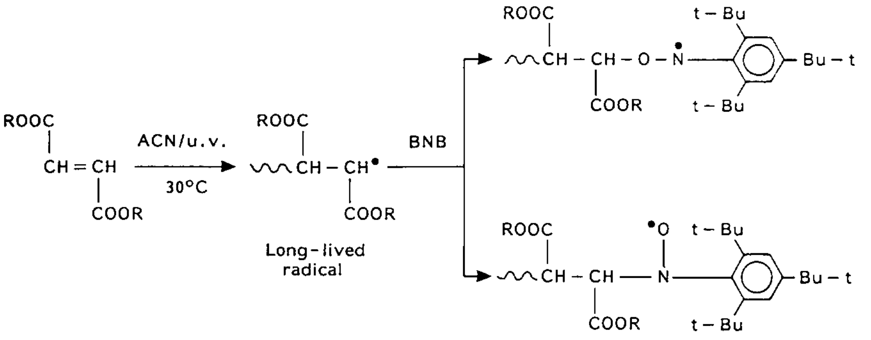


Figure 3 E.s.r. spectra of spin adducts of BNB with poly(DiPF) (A), poly(DcHF) (B), poly(DtBF) radicals (C). DRF was polymerized with DBH in the presence of BNB for 60 min at 40°C: [DBH] = 0.05 mol dm^{-3} and [BNB] = 0.01 mol dm^{-3}

Table 1 Proportion of anilino radical in spin adduct produced by polymerization of DRF in the presence of BNB at 40°C: [DBH] = 0.05 mol dm^{-3}

	[BNB] = 0.01 mol dm^{-3}		[BNB] = 0.10 mol dm^{-3}	
Poly(DRF) radical	[DRF] (mol dm^{-3})	Anilino radical (%)	[DRF] (mol dm^{-3})	Anilino radical (%)
DEF	4.10	35	1.00	20
DiPF	3.30	55	1.00	30
DcHF	1.50	40	1.00	40
DtBF	1.50	60	1.00	45

propagating radical that survived in the H-shaped ampoule:



The spectrum of the spin adduct from poly(DEF) radical illustrated in *Figure 5* is readily deduced to arise from a propagating radical with one α-hydrogen atom. *Figure 6* shows the spectra of the adducts from poly(DiPF), poly(DcHF), and poly(DtBF) radicals.

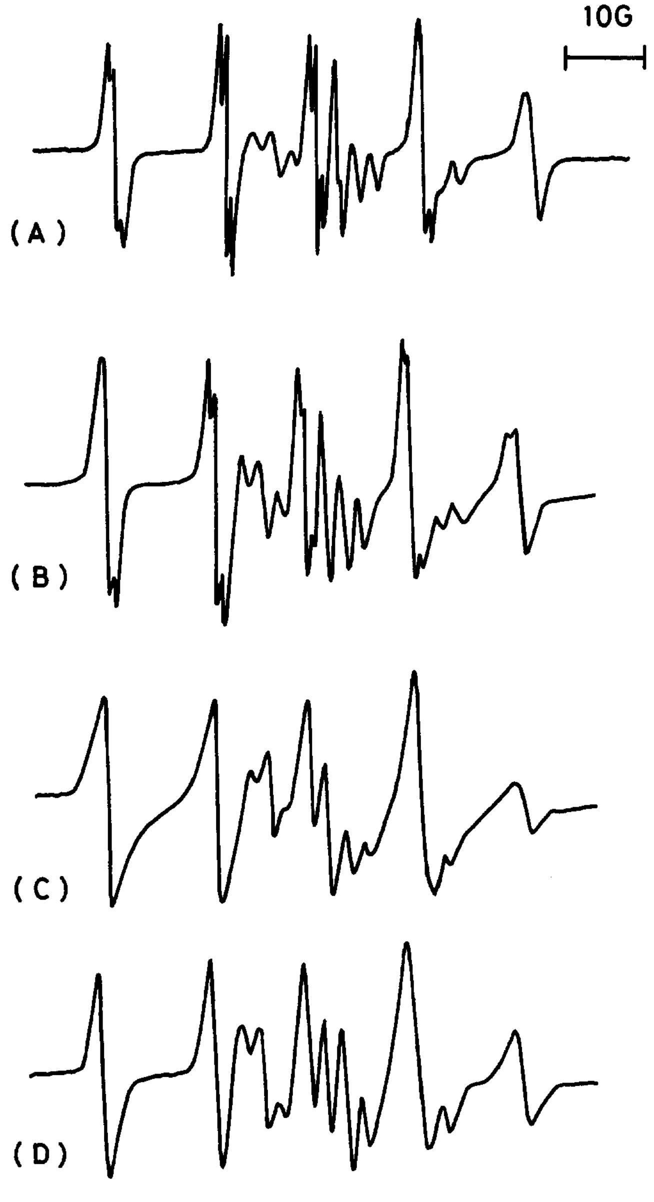


Figure 4 E.s.r. spectra of spin adducts of BNB with poly(DEF) (A), poly(DiPF) (B), poly(DcHF) (C), and poly(DtBF) radicals (D). DRF was polymerized with DBH in the presence of BNB for 60 min at 40°C: [DRF] = 1.0 mol dm^{-3}, [DBH] = 0.01 mol dm^{-3} and [BNB] = 0.1 mol dm^{-3}

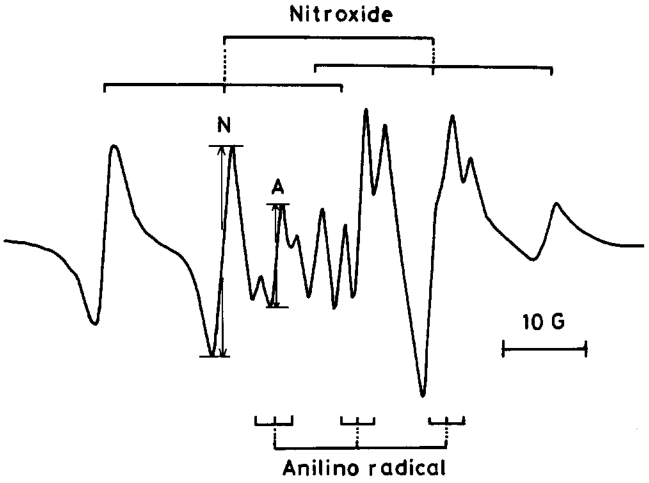


Figure 5 E.s.r. spectrum of spin adduct of BNB with poly(DEF) radical polymerized with ACN in the H-shaped ampoule under u.v. irradiation for 30 min at 30°C: [DEF] = 6.07 mol dm^{-3}, [ACN] = 0.05 mol dm^{-3} and [BNB] = 0.01 mol dm^{-3}. Splitting patterns above and below the spectrum refer to the nitroxide and anilino radical, respectively. N and A denote the signals used for comparison of the heights for estimation of the composition of the spin adduct

Since DRF was polymerized in the absence of BNB, poly(DRF) radical propagated to higher molecular weight prior to the reaction with BNB. Although all the line spacings are almost the same as those in *Figures 2* and *3*, the spectra seemed to be affected by suppressed mobility of the adduct radical in solution. The signals in the region of the spectra in these figures seem to be too weak in intensity, and the spectra recorded at higher temperatures up to 70°C tended to resemble the spectra shown in *Figures 2* and *3*. Owing to such temperature dependence, the compositions of the spectra were not determined by the simulation. Approximately, the heights of the signals of the anilino radical and nitroxide (A and N in *Figure 5*, respectively) were compared, since these signals were little affected by raising the temperature.

The ratio of the signal heights shown in *Figure 5* estimates a similar amount of the anilino radical as the spectrum in *Figure 2*. The same ratios of the pairs of signals in *Figure 6* are also likely to be similar to those of the corresponding spectra in *Figure 3*. These findings exhibit that poly(DRF) radical trapped at 0.01 mol dm^{-3} of BNB is sufficiently long to facilitate formation of the anilino radical.

Relative rate of spin trapping

The disappearance of BNB by spin trapping was followed by visible spectroscopy to determine the

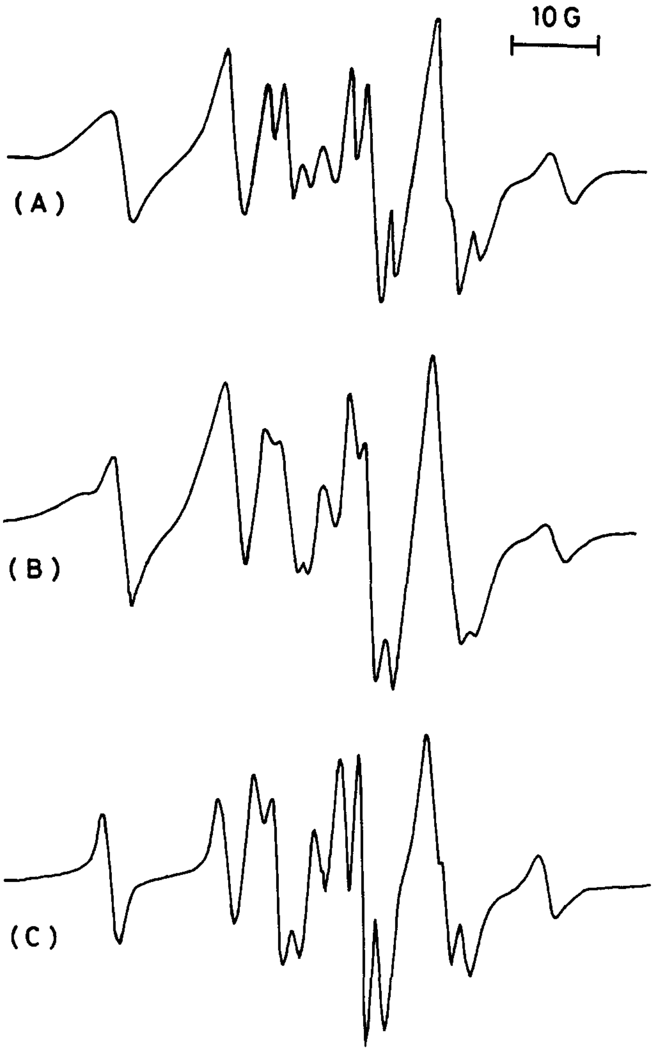
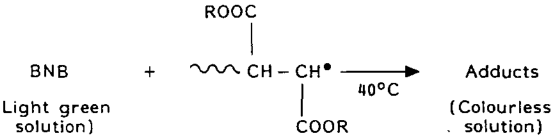


Figure 6 E.s.r. spectra of spin adducts of BNB with poly(DiPF) radical ([DiPF] = 4.94 mol dm^{-3}) (A), poly(DcHF) radical ([DcHF] = 1.50 mol dm^{-3}) (B) and poly(DtBF) radical ([DtBF] = 1.50 mol dm^{-3}) (C) polymerized with ACN under u.v. irradiation in the H-shaped ampoule for 30 min at 30°C

efficiency of the spin trapping:

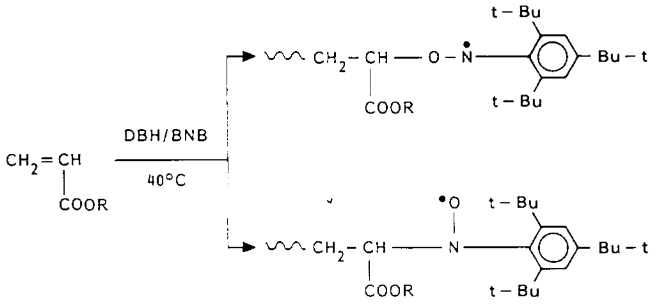


Since the absorbance at 751 nm was confirmed to remain unchanged with time in the absence of DBH or DRF, the consumption of BNB was solely caused by the reaction with the carbon-centred radical from DRF. *Table 2* shows the pseudo-first-order rate constant of the spin trap evaluated from the straight lines in *Figure 7*.

From the decomposition rate constant of DBH at 40°C[22], $k_d = 1.33 \times 10^{-5}$ s^{-1}, about 25 and 80% of the butoxy radical are estimated to be involved in the spin adduct in DEF and DtBF polymerizations, respectively, assuming the efficiency of radical production to be unity. DRF radical that was not trapped with BNB would lose activity by bimolecular termination.

Spin trapping of poly(RA) radical

The RA that gives the radical structurally resembling the poly(DRF) radical with respect to the terminal carbon was subjected to spin trapping with 0.01 mol dm^{-3} of BNB:



The e.s.r. spectrum shown in *Figure 8* was observed. The e.s.r. parameters for the nitroxide (g = 2.0057– 2.0060), a_N = 13.2, a_H = 23.5 and $a_{\mathrm{m-H}=0.9\,\mathrm{G}}$, and for the aniline radical (g = 2.0038–2.0041), a_N = 10.1 and $a_{\mathrm{m-H}}$ = 2.1 and a_H = 0.3 G were evaluated by the simulation of the spectra from the radicals of EA, iPA, cHA and tBA. The proportion of the anilino radical from poly(RA) radical (5–15%) is always less than that from the corresponding poly(DRF) radical. These findings corroborate that poly(RA) radical behaves as a less bulky radical irrespective of the chain length. Trapping in the H-shaped ampoule was impracticable for RA polymerization involving a short-lived radical. An increase in BNB concentration from 0.01 to 0.1 mol dm^{-3} did not affect the proportion of the nitroxide.

Table 2 Rate of BNB consumption by spin trapping in benzene at 40°C: [DRF] = 1.0 mol dm^{-3}; [DBH] = 0.01 mol dm^{-3}; and [BNB] = 0.01 mol dm^{-3}

DRF	Pseudo-first-order rate constant (× 10^5) (s^{-1})
DEF	0.69
DiPF	0.93
DcHF	1.30
DtBF	2.03

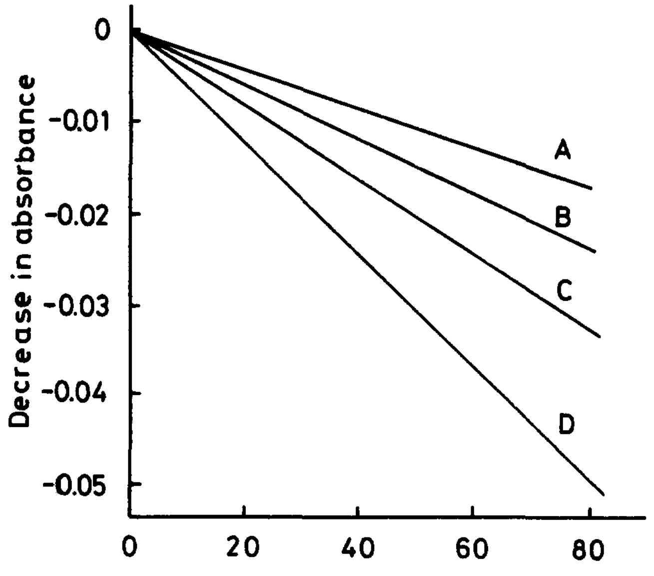


Figure 7 Decrease in absorbance of BNB by reaction with the radical produced by addition of tert-butoxy radical to DEF (A), DiPF (B), DcHF (C) and DtBF (D) in benzene at 40°C: [DRF] = 1.0 mol dm^{-3}, [BNB] = 0.01 mol dm^{-3} and [DBH] = 0.01 mol dm^{-3}

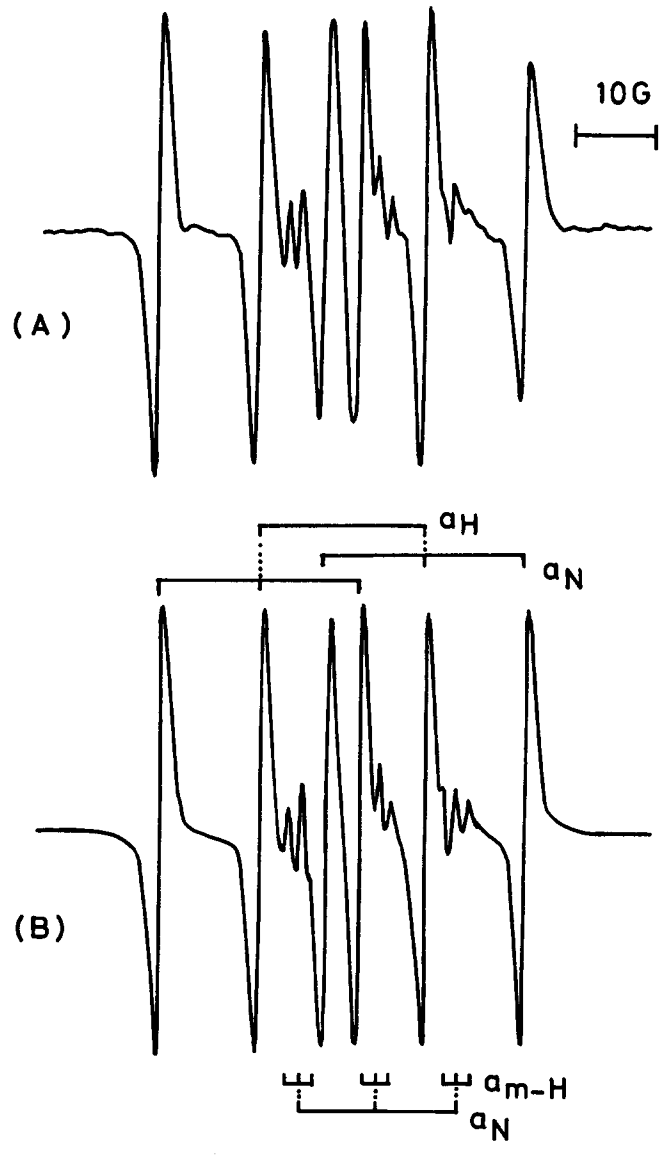


Figure 8 E.s.r. spectrum of spin adduct formed by reaction of 0.01 mol dm^{-3} of BNB with poly(EA) radical initiated with 0.05 mol dm^{-3} of DBH in the presence of BNB at 40°C (A) and computer simulation using $a_N = 13.2$, $a_H = 23.5$ and $a_{m-H} = 0.9$ G for the nitroxide, and $a_N = 10.1$, $a_{m\text{-}H} = 2.1$ and $a_H = 0.3$ G for the anilino radical (B)

Factors affecting spin trapping of poly(DRF) radical

Poly(DRF) consisting of the consecutive carboalkoxymethylene units seems to exert substantial steric hindrance on the reaction with BNB, as can be seen from the results of the spin trapping in the presence of 0.01 and 0.10 mol dm^{-3} of BNB. The spin trapping of poly(DRF) radical prepared in the H-shaped ampoule also confirmed this argument. The spin trapping of poly(RA) radical was neither affected by the chain length nor the size of the ester alkyl group.

However, the effect of the bulkiness of the ester alkyl group could not be ruled out in relation to the difference in the amount of the anilino radical at the higher BNB concentration (0.1 mol dm^{-3}), as in *Table 1*. It can be concluded that poly(DRF) radical chain and the ester alkyl group hinders the attack on the sterically congested nitrogen.

The relative rate of the spin trapping decreases in the order DtBF > DcHF > DiPF > DEF. It is anticipated that the spin trapping is in competition with bimolecular termination and that the slower termination of poly(DRF) radical with the larger alkyl groups[7,8] would cause an enhanced steady-state concentration of the polymer radical, leading to the faster consumption of BNB. Consequently, the composition of the spin adduct reflects the steric circumstances of poly(DRF) radical.

The dependence of the reactivity on chain length has been speculated from e.s.r. spectroscopic studies of poly(DRF) radicals[10]. When the polymerization was initiated with u.v. irradiation in the presence of a sensitizer, the component assignable to the lowest molecular weight appeared first, followed by the components of the longer polymer radicals. At the stationary state, the spectrum was confirmed to consist of three components and the proportion of each component was dependent on the ester alkyl group, suggesting that the chain length of the polymer radical increases with increasing size of the alkyl group. After turning off the light, decay of the spectrum was featured by the fastest disappearance of the shortest radical.

The average degree of polymerization of poly(DiPF) radical prepared in the H-shaped ampoule could be 100–500[4]. At the higher and lower concentrations of BNB and DiPF by factors of 10 and 2.47, respectively, the polymer radical should be shortened to less than one 25th, because a decrease in DRF concentration has been known to reduce substantially the molecular weight of the polymer[4]. As can be seen in *Table 1*, the adduct from poly(DiPF) radical trapped at the short chain still contains a significant amount of the anilino radical. The number of the DRF unit required to merge the steric effect of the polymer chain could be about ten. By achieving the minimum chain length, poly(DRF) would attain a fixed structure due to steric constriction, as expected from the molecular model[6]. Further extension of the chain by propagation would not affect the steric environment.

While a decrease in the termination rate constant with chain length has been ascertained in conventional radical polymerization, dependence of the propagation rate constant on chain length has not been confirmed[23,24]. Therefore the change in the reactivity with the chain length of poly(DRF) radical as observed in the present study is a unique phenomenon relating to the nature of the polymer molecule, which may arise from accumulation of the steric effects of the carboalkoxymethylene units along the main chain.

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