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Spin trapping of propagating radicals with 2,4,6-tri-*tert*-butyl-1-nitrosobenzene in radical polymerization initiated with di-*tert*-butyl hyponitrite

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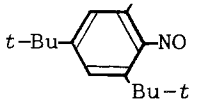
Abstract

To examine the polar effect on spin trapping with 2,4,6-tri-*tert*-butyl-1-nitrosobenzene (BNB), propagating radicals from monomers were allowed to react with BNB to provide anilino radicals and nitroxides of which the amounts were determined by ESR spectroscopy. The proportion of the anilino radical increased with an increase in the steric congestion and electron donating character of the radical. Poly(vinyl ether) radicals exclusively gave the respective anilino radicals. Poly(vinyl ester) radicals yielded large amounts (>50%) of the anilino radicals, although the nitroxides were the main products (>85%) from the poly(alkyl acrylate) radicals. The polymer radicals of methyl methacrylate and ethyl itaconate only yielded the anilino radicals. The polymer radicals from ethyl α-chloroacrylate and acrylonitrile reacted preferentially with the respective monomers leading to polymer formation, and the ESR spectra of the adducts were not observed.

Introduction

Radical polymerization has been utilized for the preparation of polymers from a wide variety of monomers. Because of the highly reactive nature and extremely low steady state concentration, the chemical behavior of the polymer radicals is often estimated relatively or indirectly. Spin trapping involving the conversion of an incipient radical to a relatively stable and ESR detectable adduct has been applied to polymerization systems (1). Among the spin trapping agents, 2,4,6-tri-*tert*-butyl-1-nitrosobenzene (BNB) has been featured by two types of adducts, a nitroxide and an anilino radical, depending on the steric circumstances of the radical center (2,3). Hence *prim*- and *tert*-radicals solely produce the nitroxide and anilino radicals, respectively. The spin trapping of a *sec*-alkyl radical, which is more and less bulkier than the *prim*- and *tert*-radicals, yields the two types of adducts.



2,4,6-Tri-*tert*—butyl-1-nitrosobenzene

(BNB)

The spin trapping with BNB has gained wide recognition in mechanistic study in polymer chemistry (4-9). However, this technique is to be used with caution because BNB reacts with the various radicals with different rates and because the spin adduct might undergo further reaction. We have disclosed the peculiarities of the steric hindrance of poly(alkyl fumarate) radicals arising from the polymer chain and the ester alkyl groups

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using BNB (10,11), and severe steric hindrance against propagation and termination resulting mainly from the polymer chain have been revealed. However, so far the reactions of BNB with limited types of polymer radicals have been studied.

BNB, which exhibits very low reactivity toward electronegative radicals (3), could exclusively trap the propagating radical in the polymerization that was initiated with an appropriate oxygen centered radical such as the *tert*-butoxy radical (*t*-BuO·). Although carbon-centered radicals with different polar characters can be derived from a variety of monomers as propagating radicals, the effect of the polar factor on the composition of the spin adduct with BNB has not been discussed except in our previous paper dealing with spin trapping of poly(styrene) and poly(*p*-substituted styrene) radicals (8). The composition of the spin adduct could suffer not only from steric effects but also from the polar effect, because of the polarization of the nitrogen-oxygen bond of the nitroso group.

The present paper is concerned with the trapping of various propagating radicals during polymerizations initiated with di-*tert*-butyl hyponitrite (DBH), and these experiments appeared to provide information on the scope of the spin trapping with BNB in radical polymerization.

Experimental part

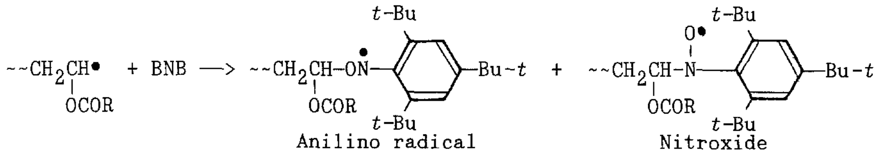
BNB and DBH were synthesized as described in the literature (12,13). Commercially available monomers, vinyl acetate (VAc), vinyl pivalate (VP), vinyl benzoate (VB), isobutyl vinyl ether (BVE), ethyl vinyl ether (EVE), acrylonitrile (AN), methyl methacrylate (MMA), ethyl itaconate (EI), and methyl crotonate (MC), were distilled under reduced pressure before use. Phenyl acrylate (PA) and 2,6-dimethylphenyl acrylate (DMPA) were prepared by reaction of acryloyl chloride with the respective sodium phenolates. Vinylene carbonate (VCa) was synthesized by dehydrochlorination of monochloroethylene carbonate (14). *N*-Acryloylpiperidine (NAPi) was prepared by reaction of acryloyl chloride with piperidine. Ethyl α-chloroacrylate (ECA) was synthesized by dehydrochlorination of ethyl α, β-dichloropropionate with quinoline.

ESR spectra were recorded on a JEOL ME 3X spectrometer with 100 KHz field modulation at X-band, and a quartz tube of 3 mm outer diameter was used. Computer simulation for the ESR spectra was performed using a program based on the procedure originally reported by Stone and Maki (15). The hyperfine coupling constant (*a*) was determined within an accuracy of ± 0.01 mT. The magnetic field and *g* value were calibrated with Mn^{2+}/MnO.

Results and Discussion

Poly(vinyl ester) radical

The polymerizations of VAc, VP, and VB were initiated with DBH at 40°C in coexistence with BNB, and the spin adducts of the respective polymer radicals were detected. The spectrum of the adduct of the poly(VAc) radical shows the presence of the anilino radical of which the *g* value is less than that of the nitroxide as shown in Fig. 1. The spin trapping of the polymer radicals of the other vinyl esters also resulted in similar spectra. Computer simulation based on the parameters and the composition of the adduct in Table 1 can reproduce the spectra.



Terabe and Konaka (2,3) have revealed the a_{H} of the anilino radicals as large as the a_{m-H}. However, the a_{H} values of the anilino radicals from the poly(vinyl ester) radicals are estimated to be smaller than the a_{m-H} as tabulated in Table 1, and the anilino radical apparently affords nine-line spectra. The a_{H} values for the nitroxides are in the range of those reported (2,3) and are smaller than the a_{m-H}. The content of the anilino radical was estimated to be at least 50% depending on the structure of the acyl group as listed in Table 2.

The results of the spin trap of the poly(vinyl ester) radicals in Table

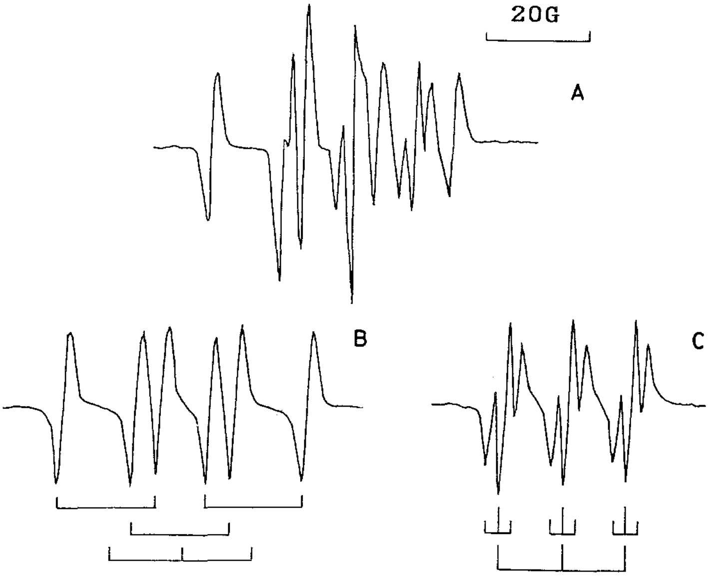


Fig. 1. ESR spectrum of the spin adduct of poly(VAc) radical. A, observed spectrum; B, computer simulation of the spectrum of the nitroxide; C, computer simulation of the spectrum of the anilino radical

Table 1. Spin adducts formed by addition of propagating radicals from vinyl ester and vinyl ether to BNB in benzene at 40°C: [DBH] = 0.01 mol/L and [BNB] = 0.05 mol/L

Monomer		Nitoroxide				Anilino radical			
	[M] (mol/L)	g value	a_{N} (mT)	a_{H} (mT)	a_{m-H} (mT)	g value	a_{N} (mT)	a_{H} (mT)	a_{m-H} (mT)
VP	4.16	2.0059	1.29	1.84	0,04	2,0031	1,06	0,04	0,22
VB	3.61	2.0061	1.24	1.67	0,09	2,0034	1,07	0,08	0.21
VAc	5.43	2.0058	1.34	1.81	0.08	2.0032	1.17	0.07	0.23
VAc a)	-	-	1.278 ±0.005	1.683 ±0.007	-	-	-	-	-
VAc b)	-	-	1.227	1.578	0.07	-	1.032	0.065	0.194
VCa	3.93	2.0062	1.30	1.73	0.06	2.0039	1.03	0.06	0.19
BVE	3.82	-	-	-	-	2.0044	1.05	0.04	0.19

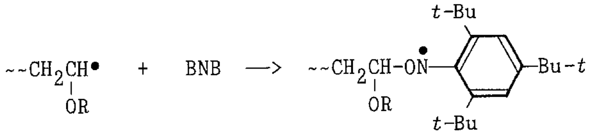
a) Ref. 4). b) Ref. 6).

2 are not in agreement with the aspects generally accepted concerning the alkyl radicals. If the composition of the spin adduct from BNB is governed solely by steric factors, all these radicals should mainly produce the nitroxide as well as the poly(acrylic ester) radicals shown later. The electron donating poly(vinyl ester) radicals that are *sec*-radicals indicate the preference of large amounts of the anilino radical.

The spin trap of the poly(VAc) radical has already been carried out in the study of regioselectivity of initiation with benzoyl peroxide. Unlike our results, Lane and Tabner (6) found that nitroxide was the sole product at higher and lower concentrations of BNB and VAc compared to the concentrations in the present study by factors of at least 4 and 5, respectively. Under these conditions, however, the radical consisting of one VAc unit with a β-benzoyloxy group could be trapped preferentially, and the electronegative β-substituent allowed to produce the nitroxide.

Poly(vinyl ether) radicals

The spin trapping of the radicals from vinyl ethers yielded almost solely the anilino radical, which was inconsistent with the expectations based on the structure of the radical center. As Fig. 2 shows, BVE/DBH/BNB system gave the nine-line spectrum which can be explained by splitting with one nitrogen and two of the *meta*-hydrogens of the anilino radical. The ESR parameters used for simulation are summarized in Table 1. Splitting by the α-hydrogen of the poly(vinyl ether) moiety is not apparent in the spectrum. All the a_{H} values of the anilino radicals were also found to be smaller than the corresponding $a_{\mathrm{m-H}}$. The spectra of the adducts from the poly(vinyl ether) radicals were recorded at a lower amplitude than the adduct from the poly(vinyl ester) radicals, and a fast reaction with BNB is expected. The adduct was not produced by heating the vinyl ether and BNB in the absence of DBH. BNB could provide a sensitive means of detecting these radicals; the size of the ether alkyl group does not reflect the proportion of the anilino radical.



Anilino radical

The electron donating substituent of the radical appears to facilitate attack on the nitrogen of BNB because of the more electronegative character of the oxygen. As a result, separation of the steric crowding effect from the polar effect on the composition of the adduct becomes obscure. The polymer radical from styrene of which the *e* value is -0.8 has been shown to yield a spin adduct consisting of 30% of the anilino radical at low con-

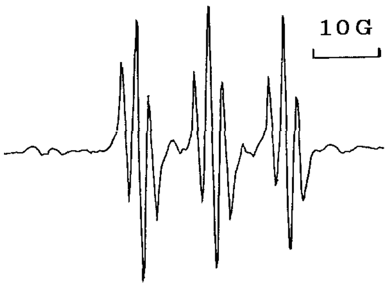


Fig. 2. ESR spectrum of the spin adduct of poly(BVE) radical

versions (4). The higher contents of the anilino radical in the adducts of the poly(vinyl ester) and poly(vinyl ether) radicals appear to be ascribable to electron donating character of these radicals.

Poly(acrylic ester) and related radicals

The electron accepting poly(acrylate) radicals mainly yielded nitroxide. In conformity with the predictions based on steric congestion, the spectra of the spin adduct of the poly(acrylate) radicals have been shown to consist of the nitroxide and small amounts of the anilino radical (10) as summarized in Table 2. As can be seen from Fig. 3, the 2,6-dimethyl substitution did not affect the composition of the spin adduct suggesting similar steric circumstances for poly(PA) and poly(DMPA) radicals. This is a reasonable trend, because the size of the ester alkyl group did not affect the relative

Table 2. Composition of the spin adduct, and *e* and *Q* values of monomers

Type of radical		Anilino radical (mol-%)	Monomer[a]		Type of radical		Anilino radical (mol-%)	Monomer[a]	
			e	*Q*				*e*	*Q*
BVE	*sec*	100	-1.77	0.023	iPA	*sec*	5[d]	0.45[e]	0.48[e]
St	*sec*	30[b]	-0.80	1.00	PA	*sec*	0	0.50[f]	0.96[f]
VP	*sec*	70	-0.75	0.037	tBA	*sec*	10[d]	-	-
VCa	*sec*	65	-0.65	0.007	EA	*sec*	15[d]	0.66[e]	0.93[e]
VB	*sec*	50	-0.55	0.061	EI	*tert*	100	0.67[g]	0.52[g]
VAc	*sec*	55	-0.20	0.026	DMPA	*sec*	0	0.90[f]	0.70[f]
NAPi	*sec*	65	-0.17[c]	0.28[c]	MC	*sec*	0	-	-
MMA	*tert*	100	0.40	0.74					

a) Ref. 16 otherwise noted. b) Ref. 8). c) Ref. 18. d) Ref. 10.
e) Ref. 17. f) Ref. 19. g) Ref. 20.

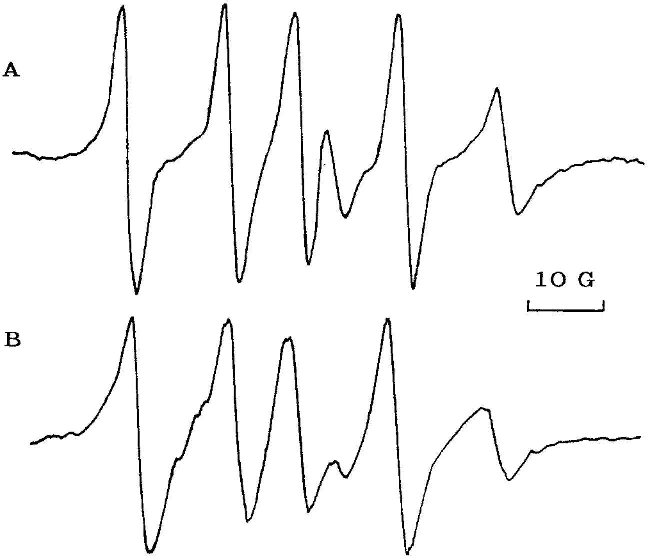
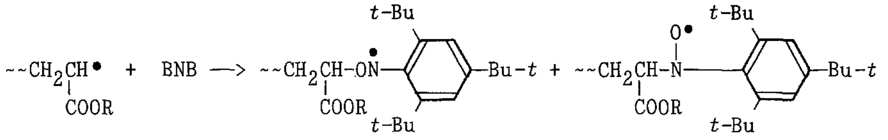


Fig. 3. ESR spectra of the spin adducts of poly(PA) radical (A) and poly(DMPA) radical (B)

reactivity of the acrylate in copolymerization (17).



Anilino radical Nitroxide

Although the formation of a large amount of the anilino radical, 65%, from the poly(NAPi) radical can be interpreted by the electron-donating character of this radical as expected from a negative e value (18), a strong tendency to retain the coplanarity of the carboxamide group is thought to sterically prefer the anilino radical formation. Neither anilino radicals nor nitroxides were detected during AN polymerization in the presence of BNB; the extremely low reactivity of the poly(AN) radical toward BNB in relation to the polar effect should be noted.

Poly(substituted acrylate) radicals

The spin adduct from the poly(MMA) radical was observed as a nine-line spectrum which is a typical splitting pattern of a triplet of a triplet assigned to the anilino radical (9). The poly(EI) radicals also produced solely the anilino radical as shown in Table 3. All these are *tert*-carbon radicals, and the steric factors caused the formation of the anilino radical.

The *e* value of ECA is the largest positive values among the monomers examined. Poly(ECA) was produced before the disappearance of BNB and explicitly showed that the polymer radical prefers to attack the monomer rather than BNB. Because the α-chloro-substituent is smaller in size than

Table 3. Spin adduct formed by addition of polymer radical to BNB in benzene at 40°C: [DBH] = 0.01 mol/L and [BNB] = 0.05 mol/L

Monomer	[M]	Nitroxide				Anilino radical			
	(mol/L)	*g* value	a_N (mT)	a_H (mT)	$a_{m\text{-}H}$ (mT)	*g* value	a_N (mT)	a_H (mT)	$a_{m\text{-}H}$ (mT)
PA	3.63	2.0065	1.35	2.29	-a)	-	-	-	-
DMPA	3.87	2.0062	1.31	2.06	-a)	-	-	-	-
NAPi	4.12	2.0061	1.34	1.70	-a)	2.0038	1.09	0.18	0.18
MMA	4.70	-	-	-	-	2.0047	0.96	-a)	0.20
MMA b)	-	-	-	-	-	-	1.002 ±0.002	0.198 ±0.0005	-
MMA c)	-	-	-	-	-	2.00394	0.959	-	0.0189
EI	3.47	-	-	-	-	2.0042	1.01	-	0.19
MC d)	3.61	2.0068	1.39	1.65	0.08	-	-	-	-
MC e)	3.61	2.0068	1.39	2.19	0.07	-	-	-	-
St b)	4.16	2.0060	1.39	1.86	0.06	2.0040	1.10	0.19	0.19
St f)	-	2.0059 ±0.0002	1.373 ±0.004	1.837 ±0.008	-	2.0036 ±0.0002	1.089 ±0.0002	0.170 ±0.0005	-
St g)	-	2.0063	1.373	1.73	0.076	2.0039	1.050	0.172	0.172

a) Too small to be determined definitely. b) Ref. 4. c) Spin adduct of polymer degradation in ref. 9. d) Spin adduct of the radical generated by hydrogen abstraction from the β-methyl group. e) Spin adduct of the radical produced by addition of the *tert*-butoxy radical to the carbon-carbon double bond. f) Ref. 8. g) Ref. 6.

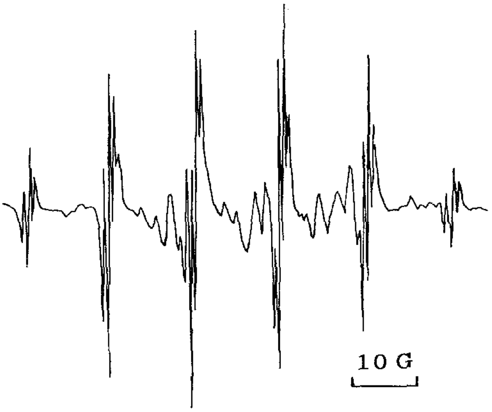
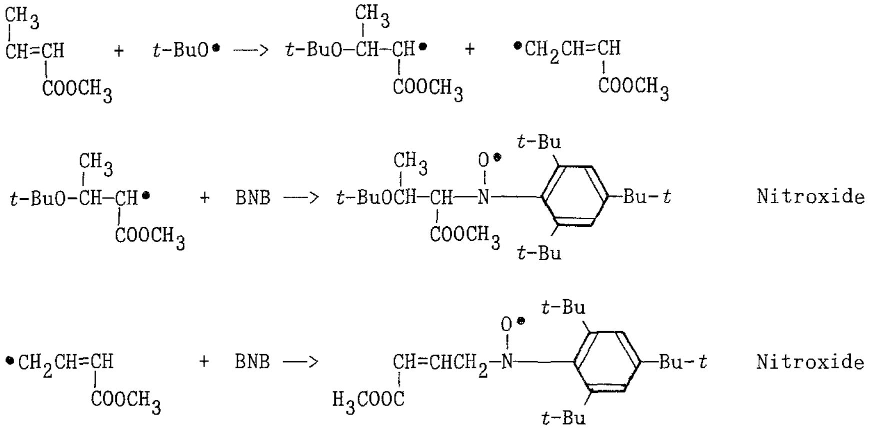


Fig. 4. ESR spectrum of the adduct of radicals generated by reactions of *tert*-butoxy radical with MC

the methyl group as estimated by steric substituent constants, E_s (21), -0.97 and -1.24, respectively, the electron-withdrawing character of the chlorine appears to slow the reaction of the poly(ECA) radical with BNB. Fast propagation of ECA (22) is also favorable for polymer formation in the presence of BNB.

When MC and BNB were heated in the presence of DBH, the complicated spectrum shown in Fig. 4 was observed. Based on the simulation, this spectrum is assignable to two types of the nitroxides. Both the substituted allyl radical generated by hydrogen abstraction from the β-methyl group and the radical formed by addition of the *t*-BuO· radical to the carbon-carbon double bond were trapped with BNB. The amounts of the anilino radicals from the *prim*- and *sec*-radicals was too small to be determined. These findings are consistent with the detection of the two types of radicals during the reaction of MC with the methyl radical using the flow technique as reported by Izumi and Ranby (23).



Conclusion

BNB was used to trap various polymer radicals. The radicals from the vinyl ethers almost exclusively produced the anilino radical regardless of the ether alkyl group. The spin trapping of the poly(vinyl ester) radicals yielded the anilino radical as the main product. These findings explicitly indicate that the anilino radical is the main product from the polymer radical with an electron-donating substituent and that the size of the ether alkyl and acyl groups actually does not affect the composition of the spin adduct.

Poly(acrylic ester) and poly(MMA) radicals produced the nitroxide and anilino radicals as their main products, respectively, in agreement with the discrimination between the *sec*- and *tert*-carbon radicals. Attempts of trap the poly(AN) and poly(ECA) radicals, which were derived from the most electrophilic monomers among the monomers employed, failed because of fast propagation and slow reaction of these polymer radicals with BNB. The peculiar steric effects observed in the dialkyl fumarate polymerization (10,11) were confirmed to be estimated appropriately without the influence of the polar effects of the substituents.

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