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Dependence of ESR spectra of poly(fumaric ester) radicals on temperature and ester alkyl group

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Summary

ESR spectra of polymer radical from fumaric esters bearing different ester alkyl groups were recorded at room temperature and 120 °C. Simulation for the spectra with much better resolution at 120 °C revealed that the spectra consist of three components differentiated by molecular weight of the polymer radical and that the component corresponding to the highest molecular weight radical increased with increasing total bulkiness of the ester alkyl groups. Gel permeation chromatography of the polymerization mixture exhibited that the radicals corresponding to the respective spectral components repeat propagation to reach high molecular weight prior to termination.

Introduction

Dialkyl fumarate (DRF) of which the substituents are expected to hinder propagation has been noted to radically homopolymerize, and an increase in the size of the ester alkyl group leads to faster polymerization to higher molecular weight [1-5]. These findings can be interpreted by the steric hindrance against propagation and termination simultaneously, and the balance of these slow elementary reactions seems to allow the polymer formation. Consistent with this argument, the polymerization of DRF has been featured by extraordinarily small rate constants for the elementary reactions and long-lived nature of the propagating radical [6-10]. Therefore, the ESR spectra of the polymer radicals have readily been observed.

While the spectra of poly(DRF) radicals consisting of broad lines were recorded at room temperature or slightly above, we have recently found that the resolution of the spectra of the polymer radicals from diethyl fumarate (DEF) and diisopropyl fumarate (DiPF) is much improved by raising the temperature to 120 °C [11]. Based on the well-resolved spectra, we have confirmed that the observed spectra consist of a triplet (T), a quartet (Q1), and a quartet (Q2), and the hyperfine coupling constants have been evaluated by computer simulation: $a_\alpha = a_\beta =$ ca. 3 G for T, $a_\alpha =$ ca. 3 and $a_\beta =$ ca. 15 G for Q1, and $a_\alpha =$ ca. 3 and $a_\beta =$ ca. 30 G for Q2. All the hyperfine coupling constants evaluated are likely to be variable within ±1 G. While poly(DEF) radical exhibited higher and lower proportions of T and Q2 than poly(DiPF) radical, the coupling constants of the

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individual components are not affected by the ester alkyl group.

It has been deduced that the respective components are differentiated by the chain length of the polymer radical. Since with increasing chain length, the enhanced steric hindrance around the radical center has been proved by spin trapping with 2,4,6-tri-*tert*-butylnitrosobenzene [12,13], the changes in the coupling constants might relate to the increase in the steric congestion of the growing radical.

In this paper, we deal with variation in the ESR spectra of the polymer radicals from fumaric esters with different ester alkyl groups (RR'F) by raising the temperature, and the peculiarities relating to the fumarate polymerization are discussed.

Experimental

Ethyl isopropyl fumarate (EiPF) was prepared by esterification of ethyl maleate with isopropanol followed by isomerization to the fumarate catalyzed with morpholine [3]. Ethyl *tert*-butyl fumarate (EtBF) was synthesized by reaction of ethyl maleate with isobutene catalyzed with a small amount of sulfric acid in a sealed tube followed by the isomerization. Ethyl cyclohexyl fumarate (EcHF) was prepared by reaction of ethyl fumaryl chloride with cyclohexanol. Di-*tert*-butyl fumarate (DtBF) was prepared as described in the literature [14]. 1,1'-Azobiscyclohexane-1-nitrile (ACN), methyl 2,2'-azobisisobutyrate (MAIB), and *tert*-butyl peroxide (TBP) were commercially available and were purified in ordinary manners. *trans*-Di-*tert*-butyl hyponitrite (DBH) was synthesized and purified as described in the literature [15].

All the ESR spectra were taken by a JEOL ME3X spectrometer at X band. Computer simulation for the spectra was performed by using a program based on the procedure originally reported by Stone and Maki [16]. The polymerizations of the fumarate except for DtBF in bulk or in benzene at room temperature and in chlorobenzene at 120°C were initiated with ACN under UV irradiation by a 100 W mercury lamp or TBP depending on the polymerization temperature in the cavity. Polymerization of DtBF at 120°C was carried out by heating the neat monomer containing TBP.

Number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) calibrated with standard poly(styrene) were measured by a Toso 8000 series HPLC equipped with columns for gel permeation chromatography (GPC) and differential refractometer (RI) was used as a detector. Tetrahydrofuran was used as eluent.

Results and Discussion

ESR spectra of the polymer radicals from some DRF's and RR'F have been reported [7-11]. In addition to these, Fig. 1 shows the ESR spectra of poly(RR'F) radicals observed during the polymerization at room temperature. Comparing these spectra with those already reported, we can speculate that DRF or RR'F polymerizing faster to higher molecular weight [4] gives the spectrum of a larger proportion of the outermost component, Q2. However, broad linewidth prevented further discussion.

Fig. 2 shows the spectrum of poly(EiPF) radical with the better resolution at 120°C and the computer simulation. The spectra of poly(EcHF) and poly(EtBF) radicals taken at 120°C are depicted in Fig. 3. Comparison of the spectra in Fig. 1 with those in Figs. 2 and 3 reveals that the resolution of the spectra are improved at the higher temperature and that the spectra at different temperatures consist of different amounts of the three components. Apparently,

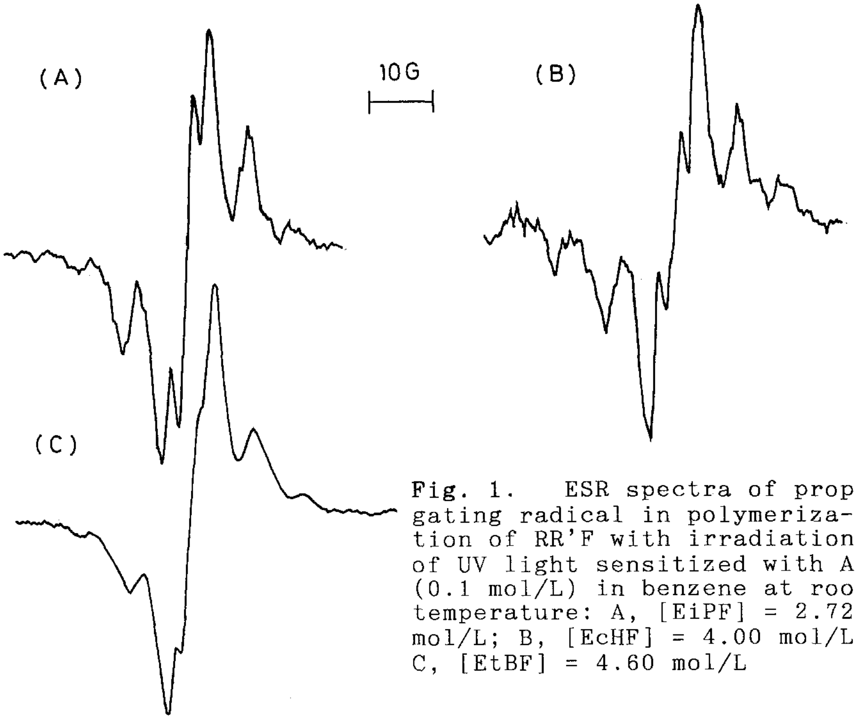

Fig. 1. ESR spectra of propagating radical in polymerization of RR'F with irradiation of UV light sensitized with ACN (0.1 mol/L) in benzene at room temperature: A, [EiPF] = 2.72 mol/L; B, [EcHF] = 4.00 mol/L; C, [EtBF] = 4.60 mol/L

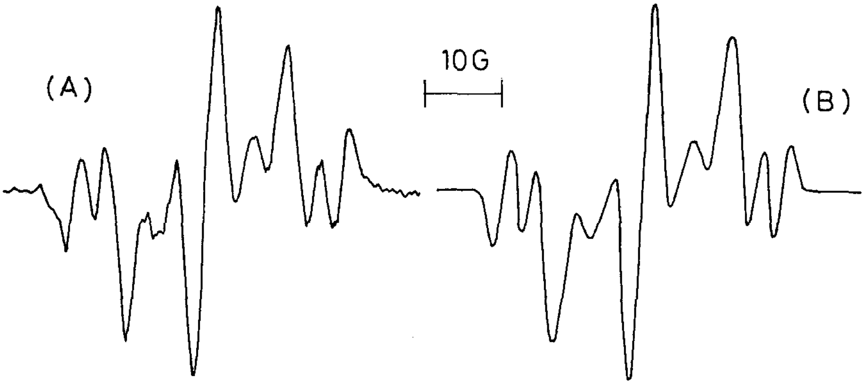

Fig. 2. ESR spectrum of poly(EiPF) radical in chlorobenzene at 120°C (A) and computer simulation (B)

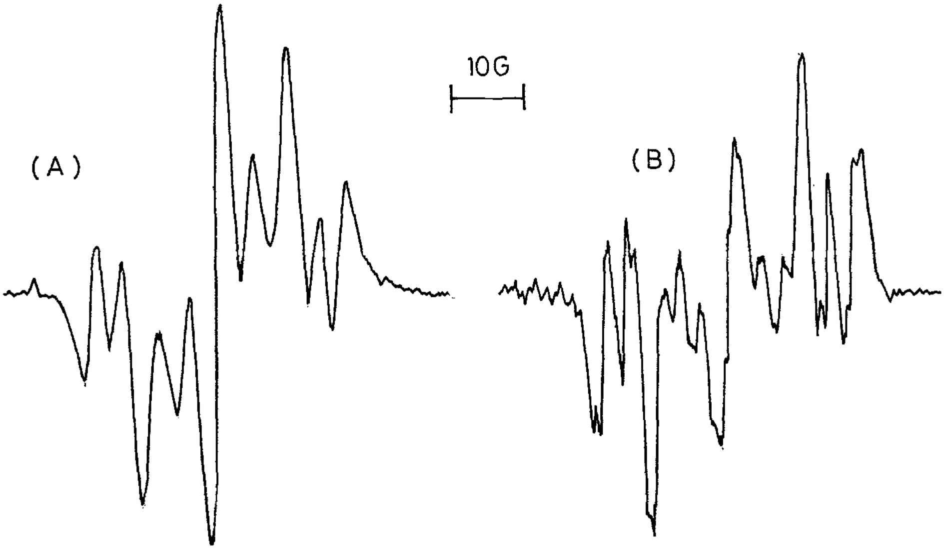

Fig. 3. ESR spectra of poly(EcHF) (A) and poly(EtBF) radicals (B) in chlorobenzene at 120°C: [TBP] = 0.27 mol/L

Table 1. ESR spectra of poly(DRF) and poly(RR'F) radicals at different temperatures

[Fumarate] (mol/L)		[I] (mol/L)	Temp. (°C)	Composition a) (%)		
				T	Q1	Q2
DEF	2.72	ACN 0.10	r.t.	85	15	-
				(2.5,3.8)	(3.0,15.0)	-
DEF b)	5.81	TBP 0.27	120	60	34	6
				(3.7,3.7)	(2.7,13.5)	(3.3,30.2)
EiPF	2.72	ACN 0.10	r.t.	82	15	3
				(2.7,3.7)	(3.7,13.3)	(3.3,30.2)
EiPF	4.25	TBP 0.27	120	48	38	14
				(3.7,3.7)	(2.7,13.5)	(3.3,30.2)
EcHF	4.00	ACN 0.10	r.t.	80	17	3
				(3.5,3.3)	(3.0,15.0)	(3.3,31.0)
EcHF	4.46	TBP 0.27	120	48	38	14
				(3.4,4.0)	(3.0,15.5)	(3.3,31.0)
DiPF b)	4.94	ACN 0.10	80	44	34	22
				(2.9,4.7)	(2.9,16.2)	(3.0,30.0)
DiPF b)	4.70	TBP 0.27	120	37	35	28
				(3.2,4.0)	(3.2,15.6)	(3.3,30.2)
EtBF	2.51	ACN 0.10	r.t.	70	22	8
				(2.5,4.5)	(3.7,14.5)	(3.6,29.0)
EtBF	4.76	TBP 0.27	120	37	39	24
				(3.0,4.7)	(2.7,16.3)	(3.2,30,0)

a) Values in the parentheses indicate the hyperfine coupling constants in G.
b) Ref. 11.

the contents of Q2 and T increased and decreased with the increase in temperature, respectively, as well as the spectra of poly(DiPF) and poly(DEF) radicals [11]. The content of T in the spectra taken at 120°C increased in the order of EtBF = DiPF < EcHF = EiPF < DEF, and the content of Q2 increased in almost the reverse order.

The hyperfine coupling constants of the each component evaluated by the computer simulation for the spectra in Figs. 2 and 3 virtually remain constants irrespective of the ester alkyl group as shown in Table 1. The coupling constants for T, Q1, and Q2 evaluated are in agree with those already reported for poly(DEF) and poly(DiPF) radicals [11]. In this table, the contents of the three components determined by the simulation are also given.

We have proposed that these compositions relate to the molecular weight distribution of the polymer radicals [11]. T and Q2 have been assigned to the polymer radicals with the shortest and longest chains, respectively, and Q1 seems to correspond to the radical of intermediate chain length [11]. Therefore, poly(RR'F) radical with larger R and R' could bring about the smaller and larger amounts of T and Q2, respectively.

Using the coupling constants evaluated with some modification, we were able to estimate the proportion of each component for the spectra at room temperature (ca. 20°C). The coupling constants and the proportions of the three components estimated are also shown in Table 1. As well as the tendency observed in the spectra at 120°C, poly(RR'F) with the larger ester alkyl groups afforded larger amounts of Q1 and Q2. The content of Q2 for poly(EiPF) radical is between those for the polymer radicals from DEF and DiPF. An increase in stiffness of the main chain arising from the large ester alkyl group is expected to suppress the termination, because of slow diffusion of the whole molecule and segment including the radical center as evidenced by the absolute rate constants for DRF [7-10]. The larger the ester alkyl group, the longer the polymer chain could be.

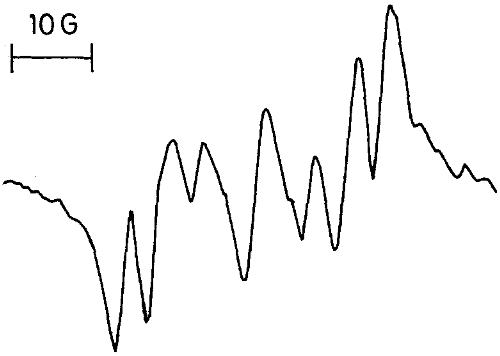

Fig. 4. ESR spectrum of poly(DtBF) radical observed during bulk polymerization in the presence of TBP at 120°C: [TBP] = 0.27 mol/L

Since no improvement in the resolution of the spectrum of poly(DtBF) radical at 120°C was observed as shown in Fig. 4, the stiff and long chain of poly(DtBF) radical could not permit to attain magnetic homogeneity of the polymerization mixture. The coupling constants and the contents of the individual components were approximately determined by the computer simulation for poly(DtBF) radical at 120°C: T (2.0 and 1.2 G), 30%, Q1 (3.5 and 17.5 G), 35%, and Q2 (4.2 and 27.8 G), 35%.

The coupling constants estimated indicate that the spectrum of poly(DtBF) radical also consists of the three components as well as poly(DRF) and poly(RR'F) radicals which gave well-resolved spectra at 120°C. In accordance with the fastest polymerization of DtBF to the highest molecular weight among the monomers used in the present work, poly(DtBF) radical is shown to contain the larger amount of Q2 than the any other polymer radicals of which the spectra are shown in Figs. 2 and 3.

Based on the well-resolved spectra, we can conclude that RR'F bearing larger R and R' polymerizing faster to higher molecular weight exhibits a higher content of the component corresponding to the higher molecular weight radicals, Q1 and Q2, at room temperature and 120°C. Since the composition of the spectrum of poly(EiPF) radical was found to be between those of poly(DEF) and poly(DiPF) radicals, the steric hindrance in the fumarate polymerization is expected to arise from total bulkiness of the ester alkyl groups. Similarly, the simulation for the spectra of poly(EcHF) and poly(EtBF) radicals having totally bulkier ester alkyl groups than two of the ethyl groups exhibits that the contents of Q2 and T are higher and lower than those of poly(DEF) radical at 120°C, respectively.

While the polymer radicals with different molecular weight presents in the DRF polymerization mixture, continuation of the polymerization yields poly(DRF). To examine the fate of poly(DRF) radicals with different molecular weight, the polymerization mixture of DEF and DiPF was subjected to GPC analysis. Fig. 5 illustrates the GPC elution curve of the DiPF polymerization mixture after the polymerization for 5 min at 120°C as an example and Table 2 summarizes the results of the GPC analyses. In this table, the conversions of the polymer and low molecular weight prodcut calculated from the elution curve, and the peak areas of the polymer, low molecular weight prodcut, and monomer were assumed to be proportional to their concentrations. Considering the uncertainity in the molecualr weight, the low molecular weight prodcut can be regarded as oligomer of DiPF or DEF.

DiPF polymerization in a sealed tube at 120°C under the comparable conditions to the ESR measurement yielded poly(DiPF) of $\bar{M}_n$ = 6900 and a small amount of oligomer corresponding to dimer. A decrease in the monomer concentration brought about a considerable decrease in $\bar{M}_n$, and the product of $\bar{M}_n$ > 1000 was not formed. Although DEF polymerization in bulk also gave poly(DEF) ($\bar{M}_n$ = 7800, M_w/M_n = 2.14) together with a small amount of the oligomer, the oligomeric product was solely formed at a lower DEF

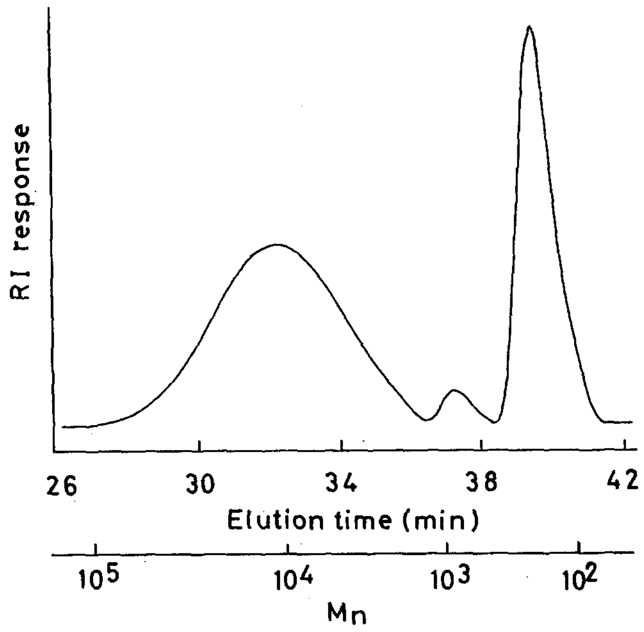

Fig. 5. GPC elution curve of the polymerization mixture of DiPF in chlorobenzene after polymerization for 2 h at 120°C: [DiPF] = 4.70 mol/L, [TBP] = 0.27 mol/L

Table 2. GPC analyses of polymerization mixture of DRF after polymerization in chlorobenzene

[DRF] (mol/L)	[Initiator] (mol/L)	Temp. (°C)	Time (h)	Polymer Convn. (%)			Oligomer Convn. (%)		
				Convn. (%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Convn. (%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
DiPF, 4.70	TBP, 0.27	120	0.08	33	6900	2.07	2	500	1.03
DiPF, 0.25	MAIB, 0.60	80	1.42	0	-	-	14	500	1.09
DEF, 6.11a)	DBH, 0.10	50	0.38	19	7800	2.14	2	400	1.05
DEF, 0.92	MAIB, 0.60	80	3.60	0	-	-	49	400	1.41

a) Bulk polymerization

concentration.

Considering these findings, we can note that the polymerization of DRF gives the corresponding polymer as main product and a small amount of the oligomer and that a decrease in the monomer concentration lead to a significant reduction of $\bar{M}_n$. Although the ESR spectra of poly(DEF) radicals consists of the three components, the GPC analysis manifested formation of the polymer and oligomer. Furthermore poly(DEF) was the main product when DEF was polymerized in bulk at 50°C, whereas the ESR spectrum observed during the polymerization under the comparable conditions consisted of mainly T component [11].

The presence of the oligomer in all the polymerization mixtures strongly suggests that the oligomer is produced by termination of the radical corresponding to T component. In this context, mutual and cross terminations of the radicals yielding Q1 and Q2 lead to the unimodal peak in GPC elution curve as the polymer. Since the composition of the ESR spectra exhibits the molecular weight distribution of the active polymer radical which loses its activity after repetition of propagation, the polymer can be accumulated as the stable product of DRF polymerization.

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