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ESR Study on Radical Polymerization and Its Application to Microemulsion Systems

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Summary: Well-resolved electron spin resonance (ESR) spectra of propagating radicals of vinyl and diene compounds were observed in a single scan by a conventional CW-ESR spectrometry without the aid of computer accumulation and the specially designed cavity and cells. Although solvents which could be used for ESR measurements were restricted to nonpolar solvents, such as benzene, toluene, and hexane, new information on dynamic behavior and reactivity of the propagating radicals in the radical polymerization of vinyl and diene compounds were obtained. Thus, values of propagation rate constants (k_p) for vinyl and diene compounds were determined by an ESR method. Some of the k_p values were in a fair agreement with those obtained by a pulsed laser polymerization (PLP) method. Furthermore, polymer chain effect on apparent k_p was clearly observed in the radical polymerization of macromonomers and in the microemulsion polymerization. In ESR measurement on inclusion polymerization system, important information on the origin of the 9-line spectrum observed in the radical polymerization of methacrylate propagating radicals was obtained.

1. Introduction

Much attention has been paid to electron spin resonance (ESR) studies of the radical polymerizations of vinyl or diene compounds, because ESR spectroscopy can theoretically provide direct information on the structures, properties, and concentrations of propagating radicals.[1,2] Usually, however, the concentration of the propagating radicals was too low to be detected in the practical conditions in

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the radical polymerization by a conventional ESR spectrometry.[1,2] More than ten years ago, we observed ESR spectra of propagating radicals for several vinyl monomers by specially designed TM Mode Cavity.[3-6] Unfortunately, we could not detect ESR spectra of the propagating radicals of styrene and diene compounds by the cavity. About ten years ago, Yamada *et al*[7] reported ESR spectra of styrene and styrene derivatives by conventional ESR spectrometer with the aid of computer. After that, we found that well-resolved ESR spectra assigned to the propagating radicals for several vinyl and diene monomers could be observed in a single scan without the aid of the computer accumulation by commercially available spectrometer, if the optimum conditions are chosen in the initiator concentration and irradiation light intensity.[8-11] In some cases of vinyl and diene compounds, the ESR measurements were possible in the steady state of the concentration of the propagating radicals if the optimum conditions are chosen in the initiator concentration and irradiation light intensity. Thus, we determined propagation rate constants (k_p) of vinyl and diene compounds by ESR method. In order to confirm the reliability of the obtained k_p values, k_p values were compared with those determined by a pulsed laser polymerization (PLP) method.[11-16] Some of them were in fair agreement with data obtained by PLP. In the extension of ESR determination of k_p, we determined k_p values for stereoregular macro-monomers and for microemulsion system, in which polymer chain effect on k_p values due to stereoregularity or aggregation was found. Furthermore, temperature dependence of well-resolved ESR spectra of propagating radical of methacrylates was investigated in the wide temperature region, clearly indicating the presence of two conformations, which are exchangeable each other. Important information on the origin of the 9-line spectrum which has been sometimes observed was obtained in the ESR measurement of the inclusion polymerization of methacrylates.

In this paper, we will mention our recent results in applications of the ESR spectroscopy to the radical polymerization system.

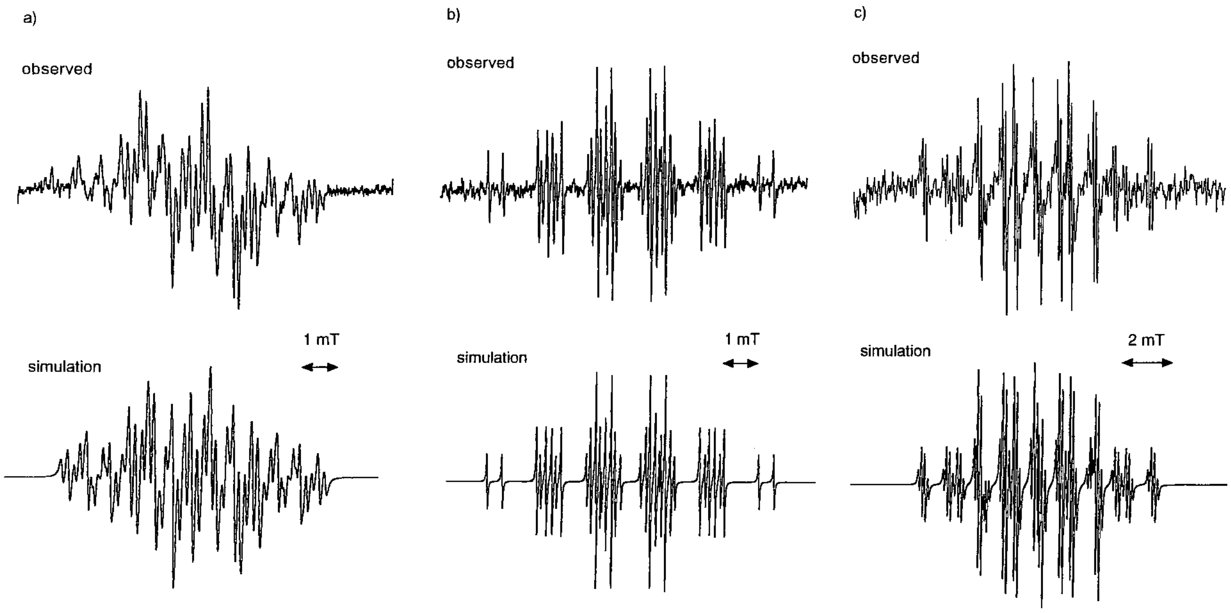


Figure 1 ESR spectra observed in the polymerization of styrene, butadiene, and MMA with Di-tert-butylperoxide under UV-irradiation, and their simulated spectra. (a) styrene (neat) at 5 °C, (b) butadiene (benzene solution) at -30 °C, and (c) MMA (toluene solution at 90℃). Spectra were observed at 0.1 mT modulation and sweep time 16 min. [*t*BPO] = 0.2 M.

2. Highly Resolved ESR Spectra of Propagating Radicals

In 1995, we found that more highly-resolved ESR spectra of propagating radicals of vinyl and diene compounds could be observed in a single scan by a conventional CW-ESR spectrometer without the aid of computer accumulation and/or the specially designed cavity and cell if the optimum condition would be chosen with regard to the concentrations of monomer and initiator, choice and the amount of solvent, the intensity of UV-light, and the diameter of sample tube.[8-10]

2.1. ESR Spectra of Propagating Radicals

Well-resolved ESR spectra were observed for radical polymerization systems of vinyl and diene compounds initiated by di-*tert*-butyl peroxide (*t*BPO), although higher initiator concentrations than that in usual radical polymerization were necessary to obtain sufficiently resolved spectra. ESR spectra taken during UV irradiation on neat styrene, butadiene, and methyl methacrylate (MMA) are shown in Figure 1.[8-11] These spectra are reasonably assigned to propagating radicals of styrene, butadiene, and MMA by simulation, respectively. Since widths of the resonance lines are narrow enough to determine accurate hyperfine coupling (hfc) values of the propagating radicals, we obtained much more detailed information about the behavior of propagating radicals as compared with that reported so far. Values of hfc for propagating radicals of diene compounds show that they are allyl type radicals in which unpaired electrons are completely delocalized.

Figure 1c shows ESR spectra for the polymerization system of MMA under UV-irradiation. The spectrum observed agrees well with that simulated by 13-line spectrum with a 0.13 mT of long range hyperfine splitting due to the ester methyl group, indicating that the more-highly resolved ESR spectrum can be observed under well-arranged conditions using conventional cavity and cell than that measured using a TM_{110}-mode cavity.[3,5] Similar 13-line spectra including long range hyperfine splitting due to γ-protons of the ester methylene group were observed for *n*-butyl methacrylate (*n*BMA), dodecyl methacrylate (DMA), and benzyl methacrylate (BzMA), although intensity distributions are a little different each other. As an example, ESR spectra taken at every 30 ° in the range from –30

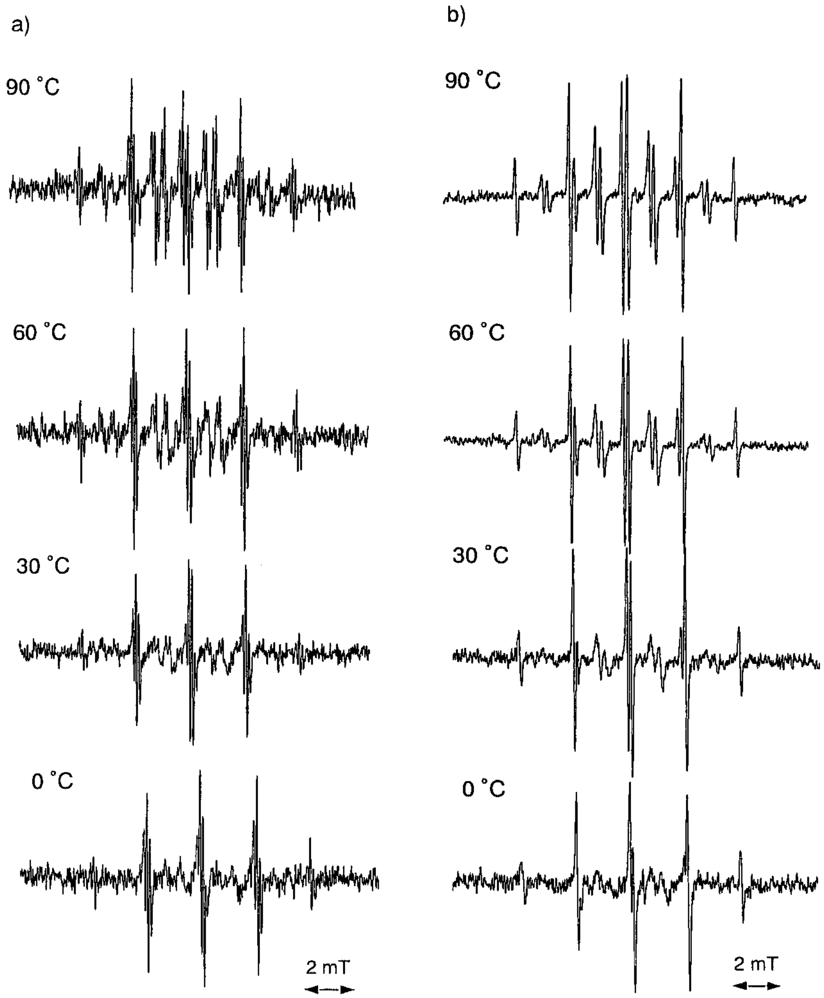


Figure 2 ESR spectra of propagating radicals of *n*BMA and *t*BMA at 90 (a), 60(b), 30 (c), and 0 (d) °C in toluene (1.5 M) initiated with *t*BPO (0.15 M) under irradiation. (0.05 mT modulation; time constant, 0.3 sec, sweep time, 16 min). (a) *n*BMA, (b) *t*BMA.

to 90 °C in solution polymerization of *n*BMA are shown in Figure 2a. The splitting pattern of these spectra was changed gradually with a change in the measurement temperature. During polymerization, the reversible change in spectra was observed at increasing and decreasing temperatures. In the case of *t*-butyl methacrylate (*t*BMA), sharper 16-line spectra shown in Figure 2b are clearly observed instead of 13-line spectra with hyperfine structure due to γ-protons. This difference is reasonably elucidated by different hfc values due to two unequivalent β-methylene protons of propagating radicals of *n*BMA and *t*BMA, caused from a variation of two dihedral angles of p-orbital-α-carbon-β-methylene carbon-hydrogens. 16-line spectra are reasonably ascribed to a doublet of doublets of quartets due to unequal β-methylene protons and α-methyl protons, in which hfc values are 1.40 and 1.16 mT for the former and 2.17 mT for the latter. Since the propagating radical of *t*BMA has no γ-protons in the ester group, ESR spectra with a larger singnal-to-noise ratio were observed in the radical

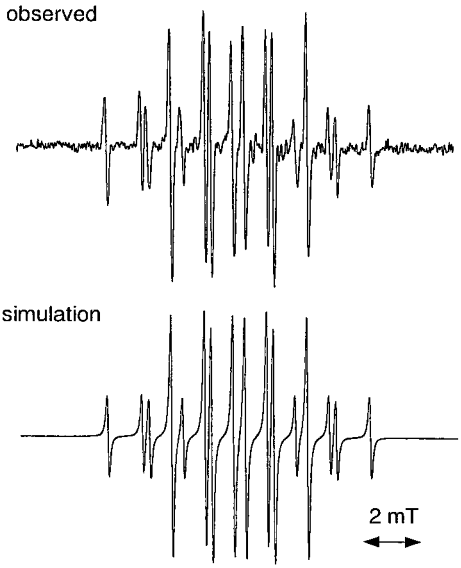


Figure 3 ESR spectrum observed in the polymerization of *t*BMA in mesitylene under UV-irradiation at 150 °C and its simulation.

polymerization of *t*BMA. As shown in the Figure 2b, the splitting pattern of spectra changes gradually with a change in the measurement temperature. These phenomena strongly suggest the presence of two exchangeable conformations. The 16-line ESR spectrum of *t*BMA obtained in mesitylene at 150 °C is simulated not only in pattern but also in intensity distribution by a single conformation (Figure 3).

ESR spectra for polymerization systems of vinyl acetate and vinyl chloride in toluene are shown in Figure 4.[16] The spectrum of vinyl acetate is reasonably assigned to the propagating radical with hfc's of 1.97, 1.75, and 1.68, and 0.13 mT for the α-proton, two β-methylene protons, and methyl protons of ester group, respectively. The resolution of this spectrum for the propagating radical of vinyl acetate is higher than that of the spectrum obtained using a TM_{110}-mode cavity.

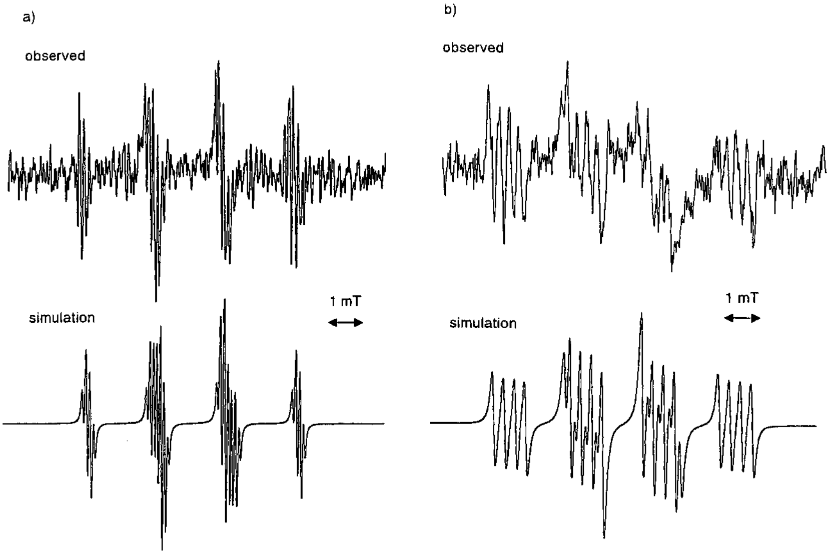


Figure 4 ESR spectra of propagating radicals of vinyl acetate (a) and vinyl chloride (b) in benzene (1.5 M) initiated with *t*BPO (0.15 M) under irradiation. (0.05 mT modulation; time constant, 0.3 sec, sweep time, 16 min).

In the case of vinyl chloride, the spectrum is reasonably assigned to be a normal propagating radical of vinyl chloride with hfc's of 1.85 (α-H), 2.00 (β-H), 2.00 (β-H), and 0.28 mT (^{35}Cl). As shown in Figure 4b, clear equivalent quartet lines due to the nuclear spin of chlorine nuclei (I = 3/2; ^{35}Cl) are observed. In principle, coupling of isotope of chlorine (^{37}Cl) should also be considered, but the spectrum was not well-resolved enough to show the difference in the hfc between the isotopes. This spectrum is reasonably simulated using these hfc values and assigned to the propagating radical of vinyl chloride.

2.2. ESR Spectra of Polymeric and Oligomeric Radicals

Resolution of ESR spectra is remarkably improved by careful measurements under well-arranged conditions, leading to the observation of much sharper spectra than those reported so far for propagating radicals. To confirm whether these spectra are really due to polymeric radicals or not, we paid attention to the fact that polymers obtained by atom transfer radical polymerization (ATRP) have C-Br bond at their chain ends.[17] Poly(*t*BMA)s of the degrees of polymerization (DP) of ca. 100 and less than 8, respectively, were prepared by ATRP, and ESR spectra of model radicals formed by C-Br bond scission of these poly(*t*BMA)s were measured in mesitylene at 150 °C under UV light irradiation. As shown in Figure 5, a 16-line ESR spectrum is observed for the poly(*t*BMA) of the larger DP, and the same spectrum as that obtained for the radical polymerization system of *t*BMA initiated by *t*BPO at the same temperature. In the case of the poly(*t*BMA) with the smaller DP, on the other hand, 12-line spectrum is observed and ascribed to a triplet of a quartet due to two equivalent methylene protons and three methyl protons, respectively. The equal hfc values of two β-methylene protons indicate that propagating radicals of *t*BMA with a smaller degree of polymerization rotate freely about the C_α-C_β bond, as in the case of vinyl ethers. These findings show that 16-line spectrum observed in *t*BPO-initiated radical polymerization of *t*BMA is due to polymeric propagating radicals. Therefore, we conclude ESR spectra observed for radical polymerization systems of vinyl and diene compounds are mainly due to polymeric propagating radicals of the corresponding monomers. GPC measurements for these polymerization systems supported this conclusion.

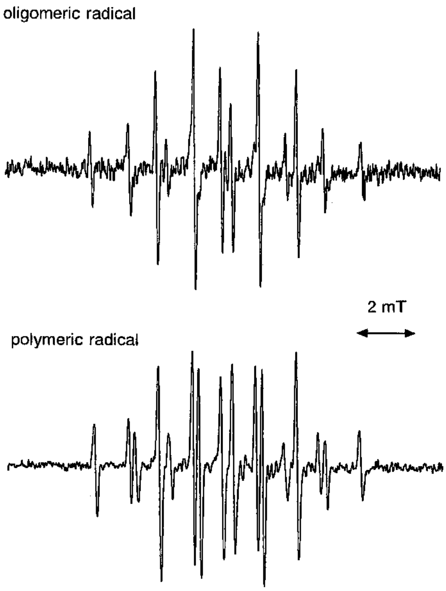


Figure 5 ESR spectra of polymeric and oligomeric radicals of *t*BMA.

3.1. Determination of k_p Values

When polymerization is started by light irradiation, ESR signals appear immediately. During polymerization, the signal intensity shows a steady-state for many vinyl and diene monomers which is confirmed on the basis of a constant signal intensity. [10-16] A steady-state can be confirmed by time dependence of signal intensity recorded, as shown in Figure 6. Steady state radical concentrations can be estimated by double integration of the spectra and calibrated with that of 3-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) in the same media.

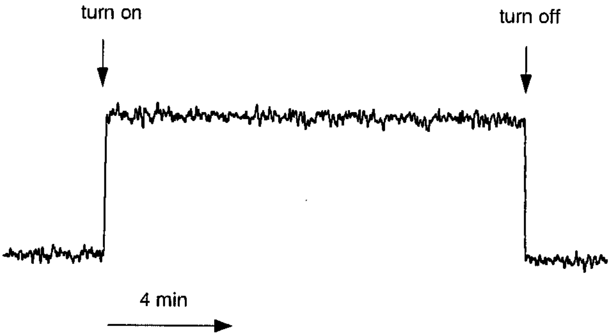


Figure 6 Time-dependence of the signal intensity of the ESR spectrum of *n*BMA at constant field.

Rate of polymerization is determined as a rate of consumption of monomer by gas chromatography. Thus, k_p is calculated by

$$R_p = -d[M]/dt = k_p[P_n\bullet][M] \qquad (1)$$

or by its integrated form

$$\ln([M]_1/[M]_2) = k_p[P_n\bullet](t_2 - t_1) \qquad (2)$$

where R_p is the rate of polymerization, [M] and $[P_n\bullet]$ are the concentrations of the monomer and propagating radical, respectively, and $[M]_1$ and $[M]_2$ are the monomer concentrations at time t_1 and t_2, respectively. A typical example of the first-order plots is shown in Figure 7.

Such a good linear relation is observed in the first order plot for the radical polymerization in benzene and toluene. Experimental error for the obtained k_p

value comes mainly from the estimation of the radical concentration. In the case of vinyl chloride, the first order plot began to deviate upward from the linear relationship at the polymerization time of ca. 3 min after initiation of polymerization by photo-irradiation.[16] Radical concentration increased from the steady concentration owing to a formation of precipitate of poly(vinyl chloride) in the sample tube, because benzene is not a good solvent for the polymer. Thus, the value of $k_p[P_n\bullet]$ was estimated from the initial slope in the first order plot and the steady concentration which was observed within several minutes after UV irradiation.

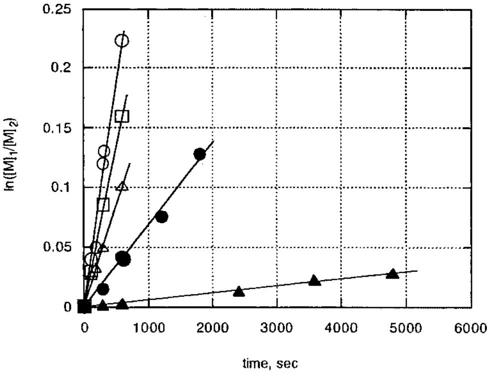


Figure 7 First-order plots for the rate of the consumption of *n*BMA during radical polymerizations at various temperatures. ○, 90 °C; □, 60 °C; △30 °C; ● 0 °C; ▲-30 °C.

Values of k_p obtained for photopolymerization of various monomers are listed in Table 1.

Table 1. Apparent propagation rate constants (k_p) of radical polymerization of monomers.

monomers	temperature, °C	k_p, $M^{-1}s^{-1}$
n butyl methacrylate	90	2000
	60	1070
	30	410
	0	220
dodecyl methacrylate	40	714
	10	321
benzyl methacrylate	40	899
	10	480
methyl methacrylate	60	500
styrene	70	450
vinyl acetate	5	4500
vinyl chloride	5	5800
1,3-butadiene	5	150
isoprene	5	125

3.2. Reliability of the k_p Values Estimated by ESR Spectrometry

Since ESR spectroscopy provides direct information about the concentration of free radicals, it seems to be an excellent method for the estimation of k_p. However, because of experimental limitations, ESR spectroscopy is a difficult technique for acquiring accurate kinetic data for some systems. To confirm the reliability of k_p values obtained by ESR spectroscopy, k_p values and Arrhenius parameters for styrene, [14] *n*BMA, [15] DMA, [12] and BzMA[13] were respectively compared with those determined by a PLP method, which constitutes the IUPAC-recommended procedure for reliable k_p measurements.[20,21] As shown in Figure 8, the rate constants and Arrhenius parameters for DMA are in fair agreement with those obtained by the PLP method. [1] Similar relation was observed in k_p values for BMA and BzMA. Reasonable agreement was found in estimated k_p values for styrene between ESR method and PLP method as shown in Figure 8b.[20] However, it should be noted here that there is a difference in k_p for styrene between ESR and PLP methods especially at a lower temperature.[14] In the case of MMA, larger difference was obtained in k_p values between both methods.[21]

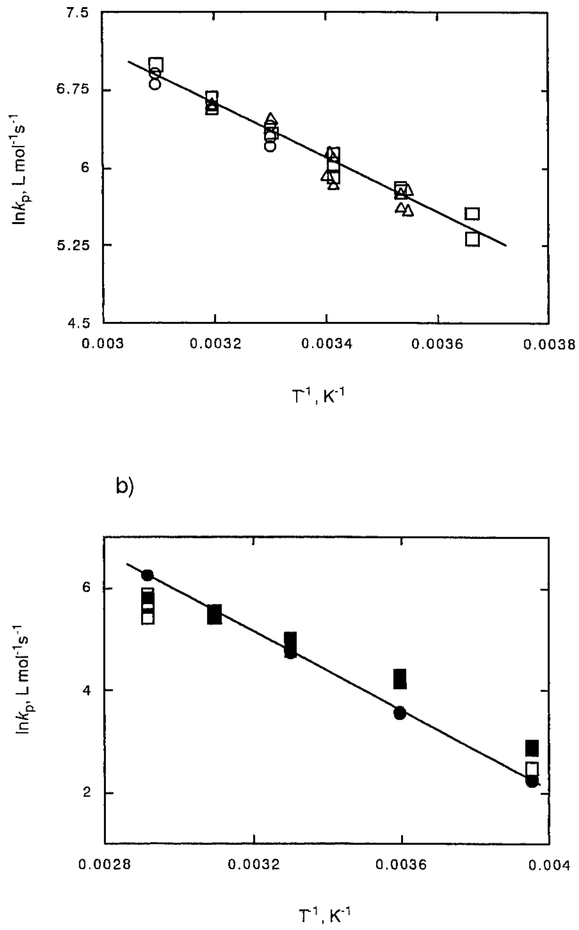
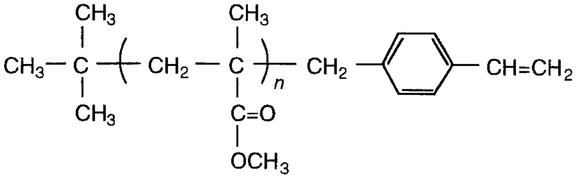


Figure 8 Temperature dependence of the propagation rate constants (k_p). (a) DMA; □, ESR data, PLP-SEC; [18] ○, PLP-SEC.[19] (b) Styrene, □, ESR data, ■, ESR data, ●, PLP data.

The k_p for vinyl chloride was determined to be 5.4 x 10^3 $M^{-1}s^{-1}$ at 25 °C with enough reproducibility,[16] although the accuracy of the k_p value seemed to insufficient because of complicated factors involved in measurements for vinyl chloride. However, the k_p value (5.4 x 10^3) agrees with one of those obtained by a rotating sector method.[22]

3.3. Polymer Chain Effect on k_p

Hatada *et al.* [23] succeeded in the preparation of stereoregular macromonomers shown in following scheme:



(3)

Glass transition temperature of syndiotactic macromonomer is much higher than that of isotactic one (Table 2), indicating that the mobility of polymer chain is much difficult in syndiotactic macromonomer than in isotactic one.

Table 2. Characteristics of *iso-* and *syn-* PMMA macromonomers

tacticity, %			M_n	M_w/M_n	CH_2=CH- per chain	T_g, °C
mm	mr	rr				
95	4	1	2900	1.12	0.96	21
1	10	89	2720	1.18	0.97	95
0	9	91	5380	1.15	0.96	105

We helped their research in the determination of rate constants by ESR spectrometry. Fortunately, we could estimated not only propagation rate constants but also termination rate constants, because signal decay after turning off the irradiation light is slow enough to estimate the termination rate constants.

The estimated rate constants along with respective polymerization rates (R_p) are shown in Table 3.

Table 3. Kinetic parameters for the polymerization of PMMA macromonomers or styrene in toluene at 60 °C with AIBN[a]

macromonomer M_n	f[b]	R_p (mol/l•s)	k_t (l/mol•s)	k_p (l/mol•s)
iso- 2900	0.28	7.4×10^{-7}	70000	50
syn- 2720	0.18	6.6×10^{-7}	670	5.2
syn- 5380	0.18	5.3×10^{-7}	590	3.9
styrene	0.7	1.9×10^{-7}	3.6×10^{7}	176

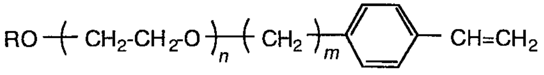
[a] $[M]_0 = 0.05$ mol/l, $[M]_0/[I]_0 = 20$ mol/mol.

[b] Initiator efficiency

Termination rate constant (k_t) for isotactic macromonomer is two orders of magnitude larger than that for syndiotactic one, and the values of k_p for the former a order of magnitude larger than that of the latter. These macromonomers are considered to be homologues of styrene. Accordingly, the estimated k_p and k_t values were respectively compared with those for styrene, indicating that they are much lower than those for styrene.

Remarkable decreases in the elementary rate constants for macromonomers are mainly ascribable for steric effect of substituents of macromonomers. The difference in the elementary rate constants between isotactic and syndiotactic macromonomers is probably due to the difference in the mobility of polymerizing chain and macromonomer, which was found in the measurement of T_g. The difference in k_p and k_t values between isotactic and syndiotactic polymacromonomers is concluded to be a polymer chain effect of stereoregular polymeric side chain on the rate constants for polymerization, because values of T_g are different in both monomers.

Ito *et al.*[24,25] have reported that polymerization rates of the following macromonomers were more than 50 times higher in water than those in benzene.



(4)

where R stands for alkyl group as an ω-end, PEO for poly(ethylene oxide), VB for p-vinylbenzyl, Cm-S for p-styrylbutyl (m=4) as α-end, and n for the number-average degree of polymerization of PEO. Since PEO-chains are soluble in water and styrylalkyl groups are insoluble in water, styrylalkyl groups organize into micelles with the polymerizing end groups locally concentrated in the cores in water. Their aggregation has been confirmed by light scattering and fluorescence probe methods. Furthermore, Ito *et al.* investigated kinetic behavior of the polymerization systems, and found that polymerization behavior followed normal kinetic dependence characteristic of the radical polymerization in water as well as

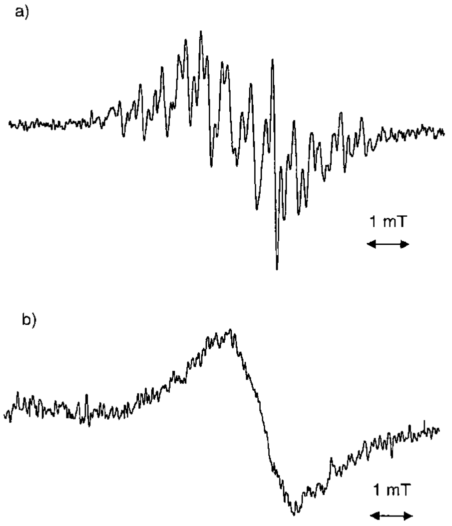


Figure 9 ESR spectra of propagating radicals in polymerizations of C1-PEO-C4-S-48 in water and in benzene. (a) [M]=50mmol/L, [*t*BPO]=2.5mmol/L in benzene; (b) [M]=50mmol/L, [4,4'-azobis(4-cyanovaleic acid)](AVA)=2.5mmol/L in water.

in benzene. For an understanding of the origin of unusually rapid radical polymerization in water, propagation and termination rate constants were estimated in water and benzene by ESR measurements.

ERS spectra of the propagating radicals of the radical polymerizations of C1-PEO-VB-48 in benzene and water are shown in Figure 9 (a) and (b), respectively.

The ESR spectrum in benzene is highly resolved and similar to that of polystyryl radical in benzene, being assigned to the propagating radical of C1-PEO-VB-48. The ESR spectrum was clearly observed in water, but it was so broad that hyperfine splitting constants could not be estimated by simulation. Broad ESR spectrum can be reasonably explained by micellar organization of the monomer in water, where the mobility of the propagating radical is restricted. Similar phenomena were also observed in ESR measurement of the radical polymerization of C1-PEO-C4-S-48. The steady state was observed in all cases, and apparent k_p values were easily estimated by the concentration of the propagating radical, and apparent k_t values by the decay of the ESR spectra upon turning off the irradiation. Results are shown in Table 4.

Table 4. Kinetic parameters of radical polymerizations under irradiation at 20 °C[a]

monomer/solvent	initiator	R_p x 10^6 mol $L^{-1}s^{-1}$	[P•] x 10^6 mol L^{-1}	k_p L $mol^{-1}s^{-1}$	k_t L $mol^{-1}s^{-1}$
C1-PEO-VB-48 /benzene	*t*BPO	3.9	2	40	1800
C1-PEO-VB-48 /water	AVA	210	4	1100	5400
C1-PEO-C4-S-48 /benzene	*t*BPO	15	5	45	4500
C1-PEO-C4-S-48 /water	AVA	510	5	2100	9000
styrene/bulk	*t*BPO	940	0.6	67 [b]	$1.9x10^7$

[a] [M] = 50 x 10^{-3} molL^{-1}, [I] = 2.5 x 10^{-3} molL^{-1} for the macromonomers, and [I] = 0.2 molL^{-1} for styrene. Values of R_p, [P•], k_p, and k_t, of the macromonomers in this work may include errors of 10-30 %. [b] Data at 20 °C from IUPAC data.

Apparent k_p values remarkably increased in water as compared with that in benzene, which was almost the same to that for bulk polymerization for styrene. The values of k_t in water were one-half or one-third those in benzene. The remarkable increase in k_p in water is probably due to organization of monomers through hydrophobic interaction of polymerizing groups, indicating that preexponential factor of k_p might increase by the organization as compared with that of k_p for styrene. The details have been discussed in Ito's paper.[24]

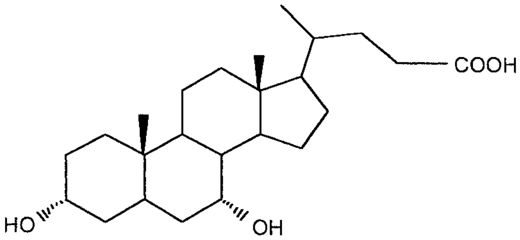
3.4. Dynamic Behavior of Propagating Radicals

More than 15 years ago, we pointed out the presence of two exchangeable conformations of propagating radicals of methacrylates and isopropenyl acetate based on results of ESR measurements for these monomers using a TM_{110}-mode cavity.[11,31] Temperature dependence of ESR spectra for MMA, *n*BMA, and *t*BMA in toluene was investigated in the temperature regime from −30 to 90 °C (Figure 2b). In the cases of *n*BMA and MMA, inner 8 lines in 13-line spectrum become broader with an decrease in the measurement temperature, and then seem to disappear. In the spectrum of *t*BMA, inner 8 lines in 16-line spectrum become broader with decreasing temperature, and then seem to disappear. During polymerization, a reversible change in the spectra was observed at increasing and decreasing temperatures. These findings show the presence of two exchangeable conformations and increase in the exchange rate with raising the temperature. To confirm this concept on the effect of temperature on the shape of spectra, ESR measurement of radical polymerization of *t*BMA was performed at 150 °C (Figure 3). The intensity of inner 8 lines of 16-line spectrum increased and sharpened, and the 16-line spectrum was simulated by a single conformation which was considered to be averaged by the rapid exchange between two stable conformations.

3.5. ESR Measurements on Inclusion Polymerization - the Origin of the 9-Line Spectra Observed in Methacrylate Radicals

In ESR measurements for radical polymerization systems of methacrylates and for poly(MMA) decomposed by irradiation of γ-ray or UV-light, 9-line spectra have been reported so far by many groups.[1,3] In our experiments, the same type of 9-line spectra was always observed in viscous polymerization systems at a high conversion, because line-width of each signal became broader in highly viscous media, leading to collapse of the inner 8 lines in 13-line spectrum or the 11 lines in 16-line spectrum into 4 broad lines, respectively. Several concepts have been proposed for the elucidation of the 9-line spectrum. In 1982, we also proposed a new concept on the basis of a change in the line shape with temperature and conformational analysis of MMA, and elucidated that these 9-line spectra are due to three types of two conformations: two stable conformations, distribution around the two conformations, and the exchange between two conformations.[26] However, it may be possible to consider that the 9-line spectra are due to propagating radicals of methacrylates with a larger DP.

Miyata *et al.*[27,28] extended their research on inclusion complex formation from diene compounds to various monomers such as methacrylates and styrene by using chemodeoxycholic acid as a host. Results are shown in Table 5.



(5)

When inclusion polymerizations of MMA and *t*BMA are performed under γ-ray irradiation, methanol-insoluble polymer is obtained from MMA, and only methanol-soluble oligomer from *t*BMA. We started colaboration on ESR study for polymerization systems of both monomers. Temperature dependence of ESR spectra is shown in Figure 10. 9-line spectra are observed in both systems.

Figure 10 shows the difference in mobility of the propagating radical between MMA and *t*BMA. In anyway, a 9-line spectrum was clearly observed in *t*BMA which was not allowed to polymerize to high polymer under the condition. This finding show that 9-line spectrum of methacrylate does not arise from polymeric radical, but also appear owing to the restricted motion of oligomeric radical.

Table 5. Inclusion polymerization to various olefinic compounds

monomer	Host:Guest (molar ratio)	yield, %[a]	M_n, x10^4	M_w/M_n[b]
styrene	1:0.7	80	13.4	3.2
2,3-dimetthyl-1,3-butadiene	1:0.8	55	4.5	2.6
methyl methacrylate	1:1.0	50	11.0	2.8
ethyl methacrylate	1:0.9	80	8.0	1.2
isopropyl methacrylate	1:0.9	0	-	-
n-butyl methacrylate	1:0.9	45	7.1	1.3
isobutyl methacrylate	1:0.8	35	6.9	1.3
t- butyl methacrylate	1:0.6	0	-	-

[a] Methanol-insoluble fractions were weighed.

[b] M_w/M_n is based on the calibration of standard polystyrene.

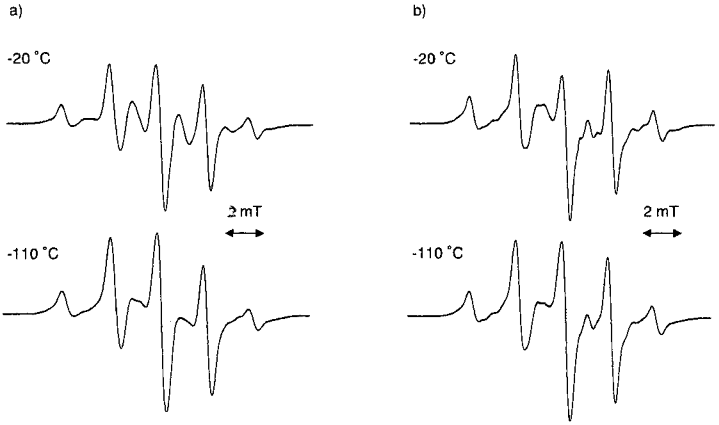


Figure 10 ESR spectra obtained in inclusion polymerization systems. (a) MMA, (b) *t*BMA

Conclusion

Well-resolved ESR spectra of propagating radicals of vinyl and diene compounds were observed in a single scan by a conventional CW-ESR spectrometry without the aid of computer accumulation and the specially designed cavity and cells. Although solvents which could be used for ESR measurements were restricted to nonpolar solvents, such as benzene, toluene, and hexane, new information on dynamic behavior and reactivity of the propagating radicals in the radical polymerization of vinyl and diene compounds were obtained. In some of them, the ESR measurements were possible in the steady state of the concentration of the propagating radicals if optimum conditions are chosen with regard to the initiator concentration and irradiation light intensity. Thus, values of k_p for vinyl and diene compounds were determined by an ESR method. Some of the k_p values were in a fair agreement with those obtained by a PLP method. Furthermore, polymer chain effect on apparent k_p was clearly observed in the radical polymerization of macromonomers and in the microemulsion polymerization. Important information on the origin of the 9-line spectrum observed in the radical polymerization of methacrylate propagating radicals was obtained.

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