ESR Study on Radical Polymerizations of Diene Compounds. Determination of Propagation Rate Constants

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ABSTRACT: Well-resolved electron spin resonance (ESR) spectra of the propagating radicals in radical polymerizations of conjugated dienes (1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 2,4-hexadiene, isoprene) have been detected for the first time by CW-ESR under irradiation without a special cavity or special techniques such as a flow method. The structures and properties of the propagating radicals of these conjugated diene compounds were investigated on the basis of hyperfine splitting constants (hfc's) of the ESR spectra. The spectra were assigned to delocalized allyl-type radicals. Moreover, the mode of addition of propagating radicals to monomer was made clear in the radical polymerization of diene compounds. The propagation rate constants (k_p) for the radical polymerization of the diene compounds were also determined by using ESR spectroscopy. Values of k_p for 1,3-butadiene, isoprene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, and 2,4-hexadiene were (150 ± 40), (125 ± 30), (35 ± 10), (20 ± 10), and (16 ± 12) $M^{-1} s^{-1}$, respectively. The difference in these values was reasonably explained by the steric repulsion between the propagating radical and the monomer and by resonance stabilization due to hyperconjugation of the methyl group.

Introduction

Although an estimation of the propagation rate constants (k_p) for the radical polymerizations of vinyl and diene compounds has been performed by several methods for an understanding of the polymerization processes, there is a large deviation among the k_p values estimated.[1] Much attention has been paid to electron spin resonance (ESR) studies of the radical polymerization of vinyl or diene compounds, because ESR spectroscopy can provide direct information on the structure, properties, and concentration of the propagating radical. Accordingly, if the steady state can be confirmed, the k_p value can be determined directly from $R_p = k_p[P_n^\bullet][M]$, where R_p and $[P_n^\bullet]$ are the rate of polymerization and the concentration of the propagating radical, respectively. Usually, however, the radical concentration at the steady state is too low to be detected by conventional CW-ESR spectrometry. Accordingly, specially designed cavities have been used for the detection of the propagating radicals. About 10 years ago, Kamachi et al. observed well-resolved spectra of the propagating radicals in the photopolymerization of several vinyl monomer such as methacrylates and vinyl esters by means of a specially designed TM-mode cavity.[2] However, they could not observe well-resolved ESR spectra of the propagating radicals of styrene and diene compounds even with the TM-mode cavity. In 1992, Yamada et al. found that an application of a computer to the ESR measurements led to higher sensitivity on ESR observation and that well-resolved ESR spectra of propagating radicals of styrene and substituted styrenes were observed at room temperature.[3]

More than 10 years ago, Kamachi et al. performed a kinetic study on the radical polymerization of diene compounds[4] and attempted ESR measurements of the polymerization system to obtain additional information on the propagating radicals.[5] Since no signal could be detected in these polymerizations in the liquid state at room temperature, ESR measurements were performed on frozen solutions. Two years ago, our preliminary report showed that well-resolved ESR spectra of the propagating radicals of diene compounds could be detected in the liquid state at room temperature aided by computer spectral accumulation.[6]

Moreove, we recently found that well-resolved spectra could be observed even in a single scan, allowing the observation of the radical polymerization of diene compounds under steady-state conditions. To our knowledge, there have been no publications on the ESR detection of the propagating radical of diene compounds in the liquid state without special methods such as a flow method.[7] Accordingly, we applied ESR spectroscopy to the determination of the propagation rate constants of diene compounds. To our knowledge, only a few studies have so far been reported on the determination of the propagation rate constants for the radical polymerization of diene compounds.[1] The k_p for diene compounds has been estimated using the Smith−Ewart theory of emulsion polymerizations[8] and the pulsed-laser polymerization (PLP) method.[9] Since the ESR method gives direct information on the establishment of a stationary state and the radical concentration, we consider that the ESR method can provide a more reliable value of k_p.

In this paper, we systematically investigated the radical polymerization behavior of aliphatic diene compounds by ESR spectroscopy. Well-resolved ESR spectra of the propagating radicals of diene compounds will be reported, and the determination of the propagation rate constants of the diene compounds will be described.

Experimental Section

Monomers were purified by distillation. Dienes were polymerized in bulk with di-*tert*-butyl peroxide (*t*BPO) under UV irradiation in an ESR spectrometer with a DVT2 variable-temperature accessory. Monomer and initiator were put into a sample tube (outer diameter: 5 mm), and the solution was purged using argon gas. ESR spectra observed in the initial stage of polymerization were recorded on a JEOL JES RE-2X spectrometer operating in the X-band, utilizing a 100 kHz field modulation and a microwave power of 1 mW. A TE_{011} mode cavity with a light-irradiation window was used. Polymeriza-

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tions were carried out by irradiation at 5 °C with a 500 W ultrahigh-pressure mercury lamp (Ushio USH-500D) at a distance of ca. 15 cm from the tube in the cavity. The irradiation area of the sample solution in the cavity was estimated to be 2 cm high by using photosensitive paper. The sample solution was put in the tube within the irradiation area. k_p did not depend upon the intensity of irradiated light. When we decreased the intensity with a filter, both the concentration of the propagating radical and the rate of polymerization decreased to give the same k_p. The spectra were recorded over a magnetic field range of 15 mT, the time constant of the spectrometer was 0.1−0.3 s, and the sweep time for each scan was 8−32 min. Computer simulations of the spectra were performed on a JEOL ESPRIT 330 ESR data analysis system using a Lorentzian line shape.

The steady-state concentration of the propagating radical was measured by double integration of the ESR spectrum and calibrated with that of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPOL) in the same media. The calculations were carried out on the ESPRIT 330 (JEOL).

The weight-average molecular weight ($\bar{M}_w$) of the polymerized products was roughly estimated from GPC measurements in THF with a TOSOH CCP&8010 series GPC system equipped with UV and RI detectors and calibrated with standard polystyrenes.

The rate of polymerization R_p was estimated as the rate of decrease of the monomer concentration. A very small amount of the polymerization mixture was sampled from the irradiated ESR tube and checked by gas chromatography with a Shimadzu GC-6A gas chromatograph using silicone DC-550, which was calibrated with either a toluene or a hexane standard. In the case of 1,3-butadiene, R_p was determined from the decrease in the signal intensity of the monomer by ^{1}H-NMR spectroscopy with a JEOL JNM EX-270 spectrometer at 5 °C. 1,3-Butadiene was dissolved in deuterated benzene (C_6D_6) containing a given amount of benzene (C_6H_6) as an internal standard.

Results and Discussion

Structure of Propagating Radicals. Although we have reported in a previous paper that the ESR spectra of the propagating radical can be observed by repeated accumulations for 100−300 scans with the aid of a computer,[6] we recently found that well-resolved spectra can be observed even with a single scan at room temperature by the careful control of the measurement conditions: concentrations of monomer and initiator, amount of solvents, intensity of the Hg light, and diameter of the sample tube. Well-resolved ESR spectra were observed in the radical polymerization of the diene compounds with *t*BPO, although higher initiator concentrations (5 mol % for monomer) than that in usual radical polymerization were necessary to obtain sufficiently resolved spectra to investigate the behavior of the propagating radical. ESR spectra taken during UV irradiation on neat 1,3-butadiene, 2,4-hexadiene, 2-methyl-1,3-pentadiene, and isoprene containing 5 mol % of di-*tert*-butyl peroxide (*t*BPO) are shown in Figures 1A−4A. The propagating radical has been observed by a rapid flow method in aqueous solution,[7] in a solid matrix at very low temperature under γ-ray irradiation,[10] or indirectly by the spin-trapping method.[11] We succeeded in observing a well-resolved spectrum of the propagating radical of 1,3-butadiene without repeated accumulation owing to advances in the standard JEOL ESR spectrometer and careful optimization of the conditions of polymerization. This spectrum was satisfactorily simulated by using proper hyperfine splitting constants (hfc's), as shown in Figure 1B. The characteristic point of this simulation is the same coupling constant due to two protons attached to both sides of the allyl structure (Chart 1 and Table 1). From the coupling constants, we can conclude that the propagating radical is a delocalized allyl type radical. In 1967, Yoshida and

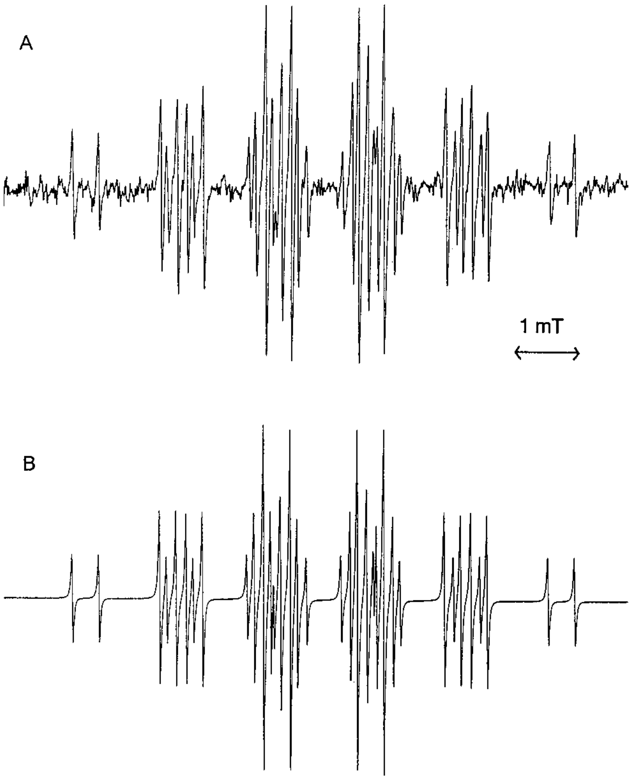


Figure 1. ESR spectrum of the propagating radical of 1,3-butadiene observed at −30 °C: (A) observed spectrum at 0.025 mT modulation and 1 scan (16 min) (neat); (B) computer-simulated spectrum.

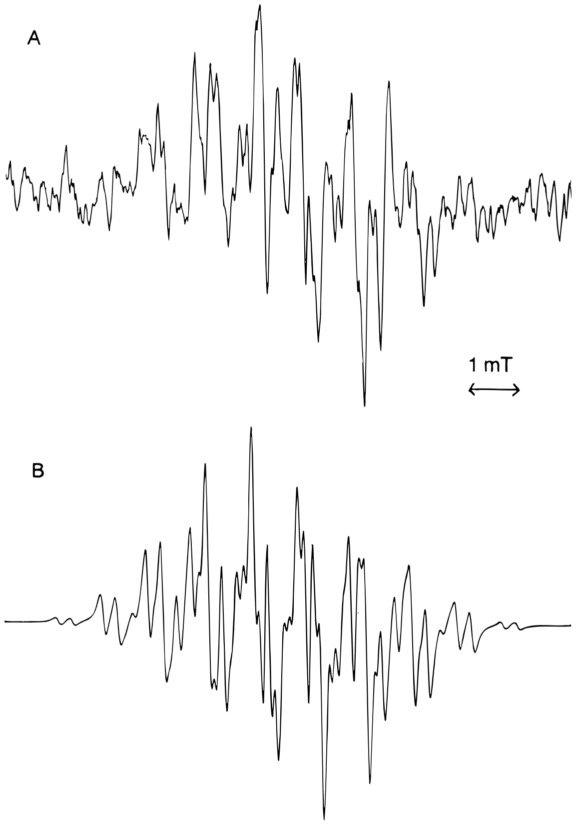


Figure 2. ESR spectrum of the propagating radical of 2,4-hexadiene observed at 20 °C: (A) observed spectrum at 0.125 mT modulation and 1 scan (16 min) (neat); (B) computer-simulated spectrum.

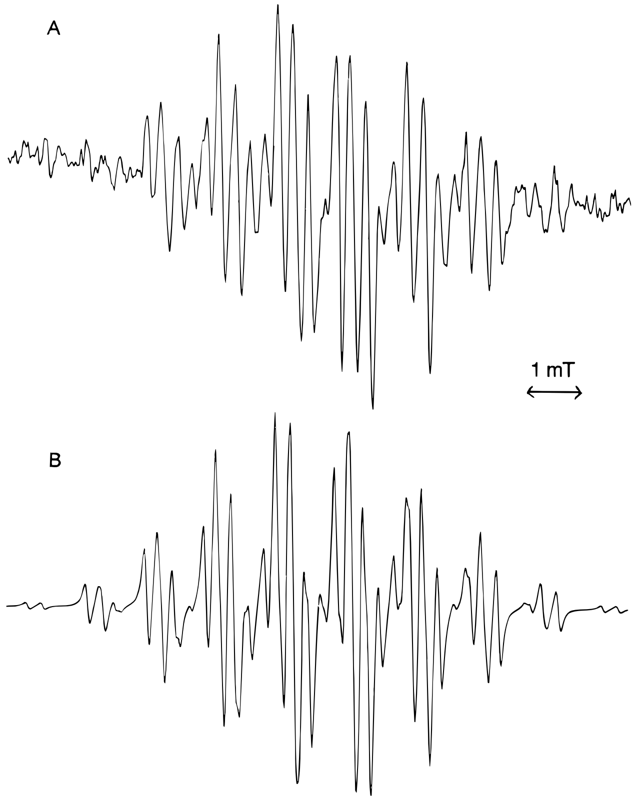


Figure 3. ESR spectrum of the propagating radical of 2-methyl-1,3-pentadiene observed at 20 °C: (A) observed spectrum at 0.125 mT modulation and 1 scan (16 min) (neat); (B) computer-simulated spectrum.

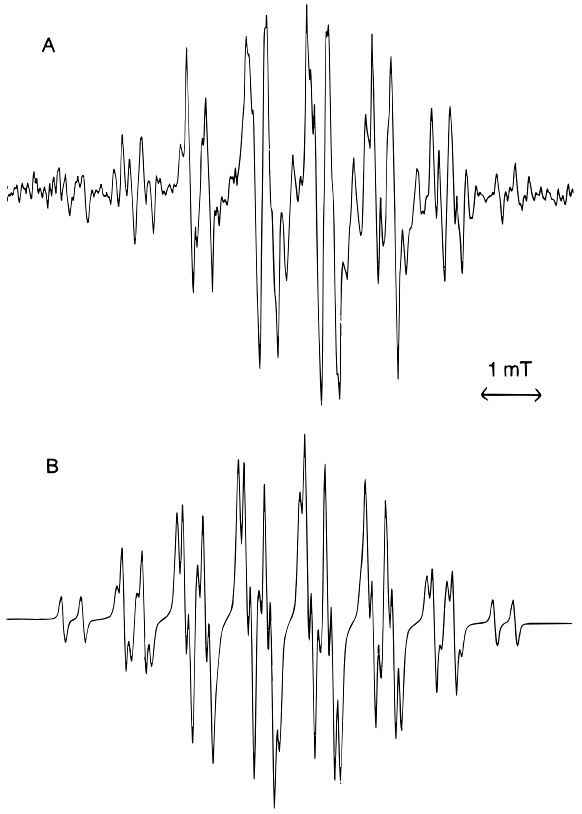


Figure 4. ESR spectrum of the propagating radical of isoprene observed at 20 °C: (A) observed spectrum at 0.125 mT modulation and 1 scan (32 min) (neat); (B) computer-simulated spectrum.

Chart 1

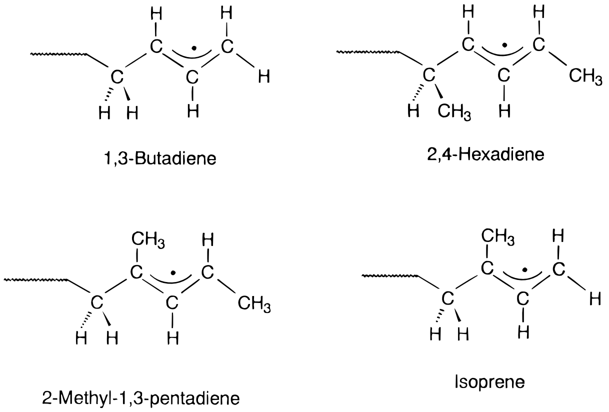
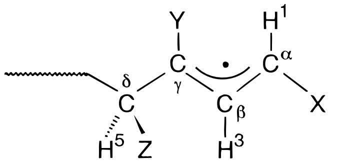


Table 1. Hyperfine Splitting Constants (mT)[a]



diene	a_{H^1}	a_X	a_{H^3}	a_Y	a_{H^5}	a_Z
1,3-butadiene	1.605	1.461	0.412	1.605	1.350	1.353
2,4-hexadiene	1.30	0.95	0.30	1.30	1.10	0.95
2-methyl-1,3-pentadiene	1.50	1.25	0.31	1.25	1.60	1.50
isoprene	1.31	1.29	0.43	1.29	1.42	1.17
allyl (ref 13)	1.48	1.38	0.41	1.48		

[a] Butadiene: X = H; Y = H; Z = H. 2,4-Hexadiene: X = CH_3; Y = H; Z = CH_3. 2-Methyl-1,3-pentadiene: X = CH_3; Y = CH_3; Z = H. Isoprene: X = H; Y = CH_3; Z = H.

Rånby observed short-lived free radicals formed by addition of HO$^•$ to 1,3-butadiene in aqueous solution by means of a rapid flow method.[7] Although the pattern of the spectrum is very similar to that of our spectrum, hfc's due to non-allyl protons of butadiene of our signal are larger than those reported by Yoshida and Rånby. Usually, hfc's of the polymeric radicals are found to be different from thos of the monomeric radicals.[12] These differences are considered to be due to the difference of the chain length of the radicals. This finding shows that the ESR spectrum in Figure 1A is the spectrum of the propagating radical. The values of hfc's for several protons are summarized in Table 1 along with those of other diene compounds and the transient allyl radical.[13] Since the line width of the resonance lines is narrow enough to estimate accurate hfc's of the propagating radicals, we were able to get much more accurate information on the behavior of the propagating radicals as compared with those in the frozen state.[5]

In the case of 2,4-hexadiene (Figure 2), the simulation also indicates the formation of an allyl-type propagating radical, because the hfc of the α-proton (1.30 mT) is the same as that of the γ-proton and the hfc of the β-proton (0.30 mT) is close to that in butadiene.

The values of the hfc's of 2-methyl-1,3-pentadiene (Figure 3 and Table 1) show that an unpaired electron in the propagating radical is delocalized in an allylic form, because the hfc due to the α-methyl protons is in agreement with that due to the γ-methyl protons and the hyperfine structure due to the β-proton of the allyl-type radical is observed in the ESR spectrum.

In the case of isoprene, the doublet of 0.43 mT shows the presence of an allylic β-proton, and the hfc of 1.29 mT is due to four protons with equal couplings, due to three methyl protons bound to a γ-carbon and one α-methylene proton. The hfc's of isoprene (Figure 4 and

Scheme 1

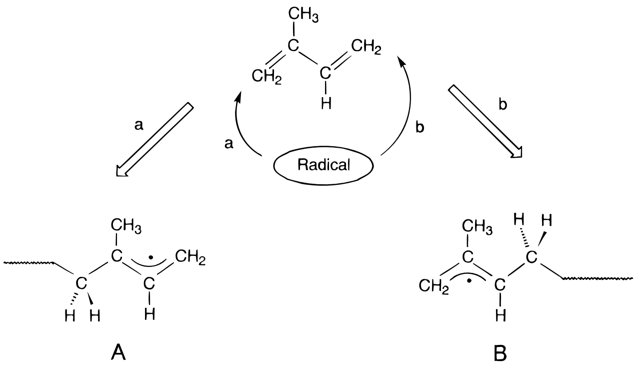


Table 1) also showed formation of a delocalized allyl-type structure.

Two possibilities (a and b attacks in Scheme 1) are considered in the attack of initiator radicals to unsymmetrical diene compounds such as isoprene. Since there is no allylic β-proton in the B-type structure, we can conclude that the propagating radical has the A-type structure in Scheme 1. This finding shows that radical attack on isoprene mainly takes place at the 1-position of isoprene. The reason why attack at the 1-position of isoprene predominates over the 4-position is probably ascribable to the stabilization of the propagating radical by hyperconjugation with the methyl group.

In the case of 2-methyl-1,3-pentadiene, if the attack at the 4-position is predominant, the hfc due to the β-proton (0.3−0.4 mT) is not observed in the ESR spectrum. These findings show that radical attack is more predominant at the 1-position of the diene bond than at the 4-position. The reason why the attack at the 1-position of 2-methyl-1,3-pentadiene is more predominant is also ascribable to both the stabilization of the propagating radical with hyperconjugation of the methyl groups and the steric effect of the methyl group bound to its 4-position.

The structures of these propagating radicals of diene compounds are summarized in Chart 1.

Determination of Propagation Rate Constants (k_p). We could observe well-resolved spectra in a single scan without a computer accumulation in the liquid state as shown above after optimizing conditions for ESR measurements. Moreover, the steady state of the radical concentration in the polymerization was confirmed by the time dependence of the intensity of the ESR signal at constant magnetic field during irradiation with light (Figure 5a−d). When the sample was irradiated with light, the ESR signal rose immediately. During the irradiation, the signal intensity showed a steady state. The steady state of the radical polymerization of isoprene was observed over 30 min. When we turned off the light, the signal decayed very rapidly. Accordingly, the determination of the propagation rate constants in the radical polymerization of diene compounds was attempted by ESR spectroscopy.

The steady-state concentration of the propagating radical was measured by double integration of the ESR spectrum. The relationship between radical concentrations and the values obtained by the double integration were calibrated by solutions of TEMPOL radical dissolved in the same media. The estimated values for 1,3-butadiene, isoprene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, and 2,4-hexadiene were 2.6 × 10^{-7}, 6.3 × 10^{-7}, 6.7 × 10^{-7}, 6.0 × 10^{-7}, and 8.9 × 10^{-7} M, respectively.

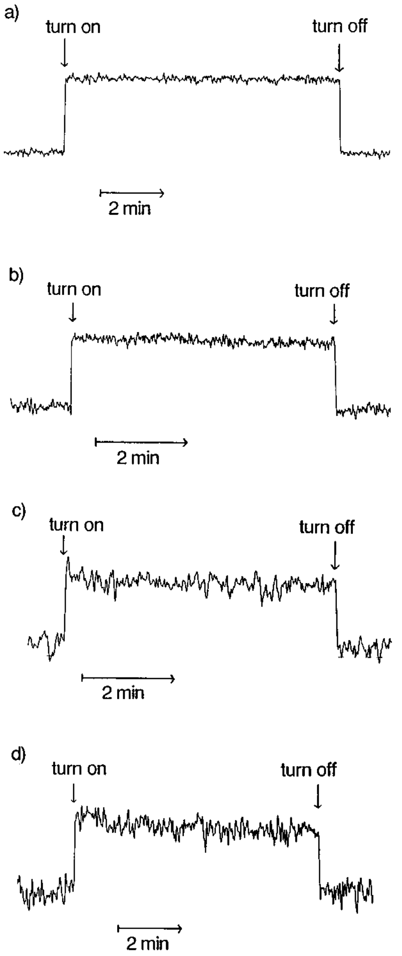


Figure 5. Time-dependence of the signal intensity of the ESR spectrum at constant field of (a) 1,3-butadiene, (b) isoprene, (c) 2-methyl-1,3-pentadiene, and (d) 2,4-hexadiene.

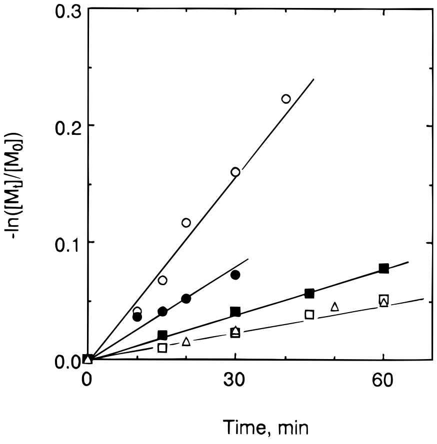


Figure 6. First-order plot of decrease in monomer concentration of dienes during radical polymerizations: 1,3-butadiene (●), isoprene (○), 2-methyl-1,3-pentadiene (■), 1,3-hexadiene (□), and 2,4-hexadiene (△).

The rate of polymerization was estimated as the rate of decrease in the monomer concentration by using gas chromatography (Figure 6). The rate was estimated below ca. 10% conversion.

From these results, the propagation rate constants (k_p) of radical polymerization were calculated by the equation

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

where [M] and $[P_n^\bullet]$ are the concentrations of monomer and radical, respectively. The values of k_p for 1,3-

Table 2. Propagation Rate Constants of Radical Polymerization of Diene Compounds Initiated by Di-*tert*-butyl Peroxide under Irradiation at 5 °C

monomer	k_p, M^{-1} s^{-1}	Q
1,3-butadiene	(150 ± 40)	1.70
isoprene	(125 ± 30)	1.99
2-methyl-1,3-pentadiene	(35 ± 10)	
1,3-hexadiene	(20 ± 10)	
2,4-hexadiene	(16 ± 12)	
styrene	(180 ± 10)	1.00

butadiene, isoprene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, and 2,4-hexadiene were determined to be (150 ± 40), (125 ± 30), (35 ± 10), (20 ± 10), and (16 ± 12) M^{-1} s^{-1}, respectively.

The propagation rate constants (k_p) of the diene compounds are summarized in the Table 2 along with that of styrene.[14] The orders in the k_p of dienes are reasonably explained by steric repulsion between the propagating radical and monomer and a resonance effect due to hyperconjugation of a methyl group. When the rate constants of isoprene and 1,3-butadiene are compared with that of styrene under the same conditions, the rate constants of isoprene and 1,3-butadiene are smaller than that of styrene. The Q values reported are also shown in Table 2. The Q values of isoprene (1.99)[15] and 1,3-butadiene (1.70)[15] are larger than that of styrene (1.00), indicating that the propagating radical of the 1,3-butadiene and isoprene are more delocalized than that of styrene. Generally, the rate constant of monomer whose propagating radical is more stable is smaller. Accordingly, the smaller rate constants of 1,3-butadiene and isoprene than that of styrene is reasonably explained by the stabilization of the propagating radicals.

The k_p for isoprene was reported to be 2.8 M^{-1} s^{-1} by Morton et al. on the basis of the Smith−Ewart theory on an emulsion polymerization method at 5 °C,[8] which is smaller than our value. We estimated the rate as the rate of decrease in the monomer concentration, while Morton et al. measured the rate by the yield of polymer. The latter might neglect the formation of soluble oligomer. In fact, the weigth-average molecular weights ($\bar{M}_w$) of the polymers in our research are in the range of 2000−4000 (GPC) and these oligomers did not give any precipitates in excess methanol. We consider that the differences in the estimation of monomer consumptions probably led to the difference in the value of k_p. Recently, the k_p for 1,3-butadiene at 30 °C was estimated to be 57 M^{-1} s^{-1} by Deibert et al. by using PLP method.[9] The value is smaller than our k_p. This difference is also due to the difference in the estimation of the polymerization rate.

Conclusions

We observed for the first time highly resolved ESR spectra of propagating radicals in the radical polymerization of diene compounds without any special cavity and special technique such as a flow method. It is clear from the hfc's that an unpaired electron of the propagating radical is delocalized in the allylic form. We determined the propagation rate constants (k_p) of the radical polymerization of 1,3-butadiene, isoprene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, and 2,4-hexadiene. The difference in k_p values among diene compounds is reasonably explained by steric and resonance effects. Moreover, the addition mode of the propagating radical to unsymmetrical dienes was discussed on the basis of the hfc's of the propagating radicals of the diene compounds.

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