Macromolecules **1993,** *26,* 7369–7371

Communications to the Editor

ESR Study on Radical Polymerizations of Diene Compounds

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Received August 24, 1993
Revised Manuscript Received October 22, 1993

Introduction. Much attention has been paid to the ESR study on the radical polymerization of vinyl or diene compounds, because ESR spectroscopy is considered to be the most promising technique for obtaining information on the propagating radical. Usually, however, the radical concentration of the steady state is too low to be detected by conventional 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 monomers such as methacrylates and vinyl esters by means of a specially designed TM-mode cavity.[1] However, they could not observe well-resolved ESR spectra of the propagating radicals of styrene and diene compounds even by the TM-mode cavity. Recently, Yamada et al. found that 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.[2]

More than 10 years ago, Kamachi et al. performed a kinetic study on the radical polymerization of diene compounds[3] and attempted ESR measurements of the polymerization system for obtaining additional information on the propagating radicals.[4] Since no signal could be detected in these polymerizations in the liquid state at room temperature, ESR measurements were performed in their frozen states. Recently, we succeeded in observing the propagating radicals of diene compounds at room temperature by means of the aid of a computer. To our knowledge, there have been no publications on the detection of the propagating radical of diene compounds in the liquid state. In this paper, well-resolved ESR spectra of the propagating radicals of diene compounds will be reported and basic information on the addition mode in the radical polymerization of diene compounds will be described.

Experimental Section. ESR spectra observed in the initial stage of polymerization were recorded on a JEOL RE-2X spectrometer at an X-band utilizing 100-kHz field modulation, and a microwave power of 10–18 mW was applied. Polymerizations were carried out by irradiation at 20 °C with a 500-W ultrahigh-pressure mercury lamp at a distance of ca. 15 cm from the tube in the cavity. The spectra were recorded over a magnetic field range of 20 mT, the time constant of the spectrometer was 10 ms, and the sweep time for each scan was 5 s. Computer simulations of the spectra were performed on a JEOL ESPRIT 330 data system, and the line shape used was Lorentzian.

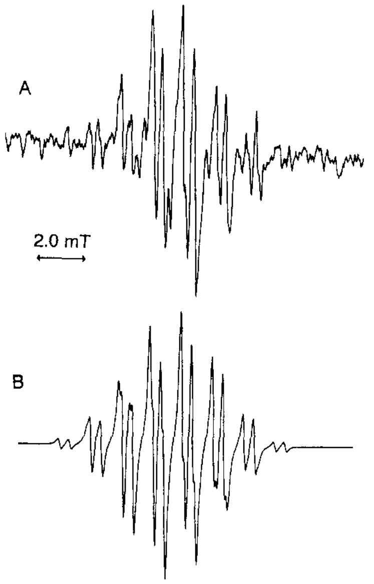

Figure 1. ESR spectrum of the propagating radical of isoprene observed at 20 °C: (A) observed spectrum at 0.125-mT modulation and 300 scans (neat); (B) computer-simulated spectrum.

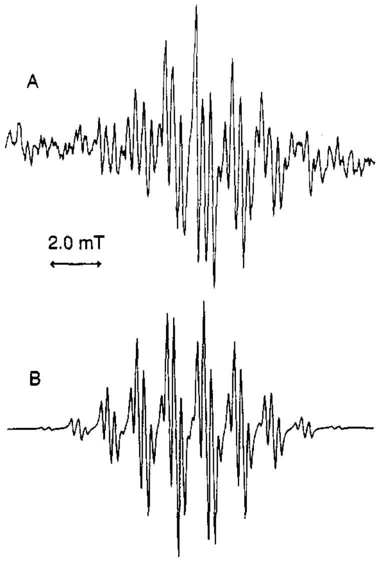

Figure 2. ESR spectrum of the propagating radical of 2-methyl-1,3-pentadiene observed at 20 °C: (A) observed spectrum at 0.125-mT modulation and 100 scans (neat); (B) computer-simulated spectrum.

Time-resolved ESR spectroscopy was carried out by the same method as described previously.[5] ESR spectra of 500 ns after laser irradiation were recorded on the basis of data stored in a LeCroy 7200 digital oscilloscope.

Results and Discussion. (a) Experiments with Di-*tert*-butyl Peroxide. ESR spectra taken during UV irradiation on a 0.5 M solution of di-*tert*-butyl peroxide (TBP) with isoprene, 2-methyl-1,3-pentadiene, and 2,4-hexadiene are shown in part A of Figures 1–3. Well-resolved ESR spectra were observed in the radical polymerization of diene compounds with TBP, although higher initiator concentrations were necessary for getting

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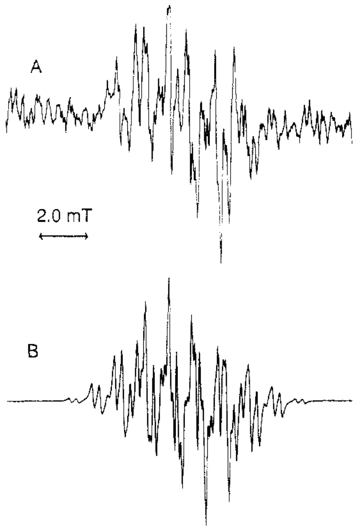
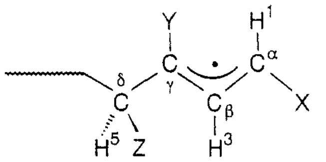


Figure 3. ESR spectrum of the propagating radical of 2,4-hexadiene observed at 20 °C: (A) observed spectrum at 0.125-mT modulation and 100 scans (neat); (B) computer-simulated spectrum.

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

diene	a_{H^1}	a_X	a_{H^3}	a_Y	a_{H^5}	a_Z	line width
isoprene	1.29	1.29	0.43	1.29	1.29	1.15	0.13
2-methyl-1,3-pentadiene	1.50	1.25	0.31	1.25	1.60	1.50	0.12
2,4-hexadiene	1.30	0.95	0.30	1.30	1.10	0.95	0.13
allyl (ref 6)	1.48	1.38	0.41	1.48			

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



enough highly resolved spectra to investigate the behavior of the propagating radical than that in the radical polymerization. The spectrum observed in the polymerization of isoprene is shown in Figure 1A as an example. This spectrum was satisfactorily simulated by using proper hyperfine splitting constants (hfc), as shown in Figure 1B. The values of hfc's for several protons are summarized in Table 1 along with those of other diene compounds and a transient allyl radical.[6] Since the line width of each resonance line is narrow enough to estimate correct hfc's of the propagating radicals, we were able to get much more correct information on the behavior of the propagating radicals as compared with that in the frozen state.[4]

The two possibilities (a and b attacks in Scheme 1) are considered in the attack of initiator radicals on unsymmetrical diene compounds such as isoprene.

In the case of isoprene, a doublet of 0.43 mT shows the presence of an allylic β-proton and the value of hfc of 1.29 mT, which is due to six protons, shows that methyl protons bound to γ-carbon, α-methylene protons, and one of the δ-methylene protons are equivalent. Since the presence of an allylic β-proton is not considered in the B-type structure shown in Scheme 1, we can conclude that the propagating radical is composed of an A-type structure in Scheme 1. This finding shows that radical attack to isoprene mainly took place at the 1-position of isoprene. The reason why attack at the 1-position of the isoprene is more predominant than that at the 4-addition is probably ascribable to the stabilization of the propagating radical with hyperconjugation of the methyl group.

Scheme 1

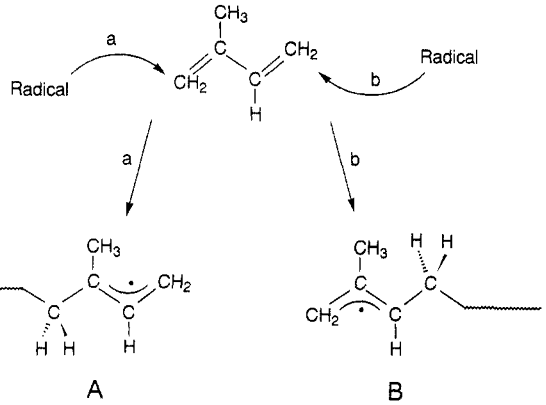
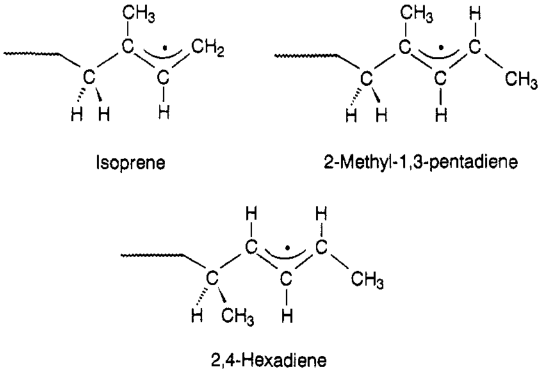


Chart 1



The values of hfc's of 2-methyl-1,3-pentadiene 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 γ-methyl protons and the hyperfine structure due to the β-proton of the allyl-type radical is observed in the ESR spectrum. 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 in the 1-position of the diene bond than in 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.

In the case of 2,4-hexadiene, 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 those in isoprene and 2-methyl-1,3-pentadiene. The structures of these propagating radicals of diene compounds are summarized in Chart 1.

(b) Experiments with (2,4,6-Trimethylbenzoyl)-diphenylphosphine Oxide. Recently, we reported a time-resolved ESR study on the initiation step of the photoinitiation of various kinds of monomers with (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMDPO), whose photodissociation yielded a 2,4,6-trimethylbenzoyl radical and a diphenylphosphinoyl radical.[5,7] We extended this research to the photoinitiation of diene compounds with TMDPO. The effect of diene compounds on the decay rate of the signals of the diphenylphosphinoyl radical and the 2,4,6-trimethylbenzoyl radical generated by the photolysis of TMDPO was investigated. While the decay rate of the diphenylphosphinoyl radical increased with

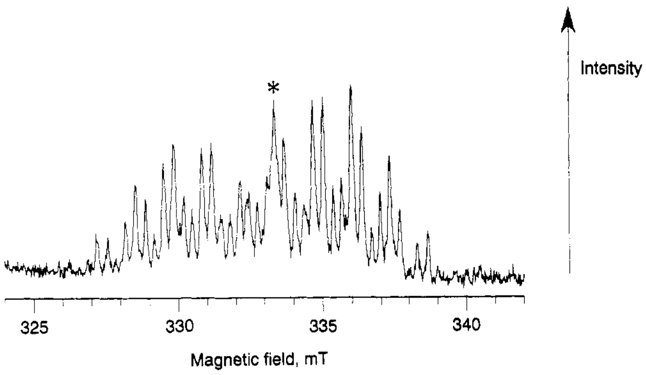


Figure 4. Time-resolved ESR spectrum observed from 324 to 342 mT after 500 ns from laser pulse irradiation of a solution of TMDPO (0.1 M) and isoprene (10 mM) in benzene. (*) 2,4,6-Trimethylbenzoyl radical.

Table 2. Rate Constants in Addition Reactions of the Diphenylphosphinoyl Radical to Diene Compounds in Benzene at 20 °C

diene	rate, $s^{-1}\ M^{-1}$
isoprene	$(1.4 \pm 0.3) \times 10^7$
2-methyl-1,3-pentadiene	$(1.2 \pm 0.3) \times 10^7$
2,4-hexadiene	$(2.9 \pm 0.3) \times 10^6$

increasing diene concentration, the decay rate of the 2,4,6-trimethylbenzoyl radical scarcely changed with increasing concentration of the monomer. This finding shows that the diphenylphosphinoyl radical is much more reactive with diene compounds than the 2,4,6-trimethylbenzoyl radical. The dependence of the decay rate of the diphenylphosphinoyl radical on the concentration of diene compounds followed first-order kinetics. Accordingly, the initiation rate constants for addition of the diphenylphosphinoyl radical to diene compounds were estimated from the relation between diene concentration and decay rate by the method previously reported.[5] The rate constants obtained are shown in Table 2.

In the measurement of time-resolved ESR spectroscopy on the photolysis of TMDPO in the presence of diene compounds, the ESR spectra after 500 ns of laser pulse irradiation were recorded by using data stored in a transient memory in the magnetic field (333 ± 10 mT). New signals along with the diphenylphosphinoyl radical and the 2,4,6-trimethylbenzoyl radical, which are obtained by the photolysis of TMDPO,[7] appeared in the magnetic field around the resonance line of the 2,4,6-trimethylbenzoyl radical. Time-resolved ESR signals detected after 500 ns of laser pulse irradiation in the presence of isoprene are shown in Figure 4 as an example. The rise and decay of one of the new signals are shown in Figure 5 along with the decay of the diphenylphosphinoyl radical. It is clear that the new signals appear more slowly than radicals produced by the photolysis of TMDPO. This suggests that the new signals are due to radicals obtained by the addition of the diphenylphosphinoyl radical to isoprene. Since the spectrum is ascribable to further splitting of the spectrum of the propagating radical by the phosphorus nucleus whose spin quantum number is $^1/_2$, it was reasonably assigned to a radical obtained by an addition reaction of the diphenylphosphinoyl radical to isoprene as shown in Scheme 2.

Conclusions. We observed highly resolved ESR spectra of propagating radicals in the radical polymerization of diene compounds. It is made clear from the hfc's that an unpaired electron of the propagating radical is delocalized in the allylic form. 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 diene compounds. Time-resolved ESR spectra of transient radicals (initiating radical) obtained by the addition reaction of the diphenylphosphinoyl radical to diene compounds were observed, and initiation rate constants were determined by the monomer concentration dependence of the decay rate of the diphenylphosphinoyl radical.

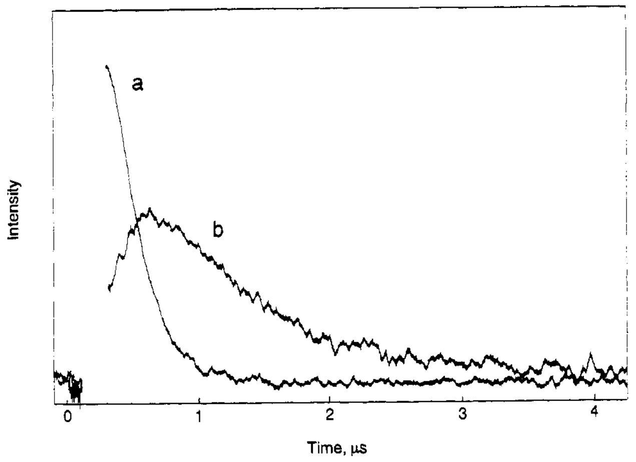
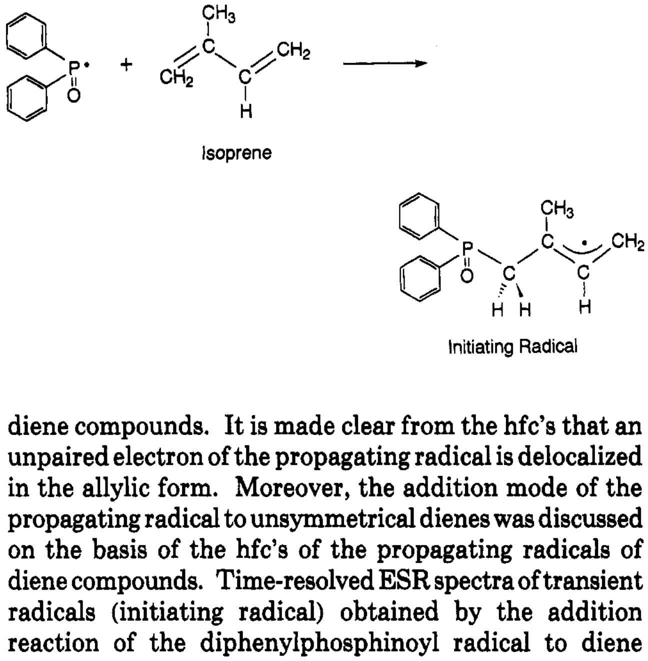


Figure 5. Time profiles of ESR signals from 300 ns to 4 μs after laser pulse irradiation: (a) diphenylphosphinoyl radical at 350.2 mT in benzene (0.1 M); (b) initiating radical at 336.0 mT. Isoprene: 0.05 M.

Scheme 2



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