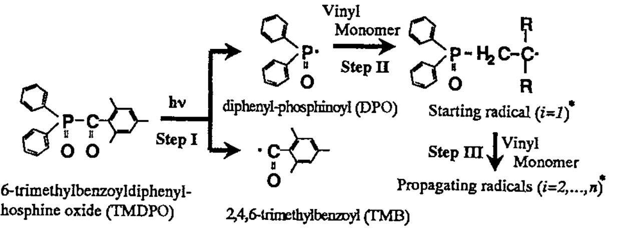
Propagating Radicals in Photo-Initiated Polymerization as Detected by Time-Resolved CW- and FT-ESR Spectroscopy

Yukio Mizuta,* Norio Morishita,† and Keiji Kuwata††
ESR Application Laboratory, JEOL LTD., Musashino, Akishima, Tokyo 196-8558
†Japan Atomic Energy Research Institute, Watanuki, Takasaki, Gunma 370-1292
††Professor Emeritus of Osaka University, Machikaneyama, Toyonaka, Osaka 560-0056

(Received December 25, 1998; CL-980951)

The primary propagating radicals in photo-initiated polymerization of isoprene and MMA were directly detected and assigned for the first time by use of time-resolved ESR spectroscopy. Based on the kinetic analysis including the spin-lattice relaxation, the rate constant of the formation and the relaxation time were determined for the primary propagating radicals by simulating time- profile of the FT-ESR intensity.

Recently, acylphosphine oxides have been developed as new photo-initiators, showing photocuring compositions.[1,2] The compound, 2,4,6-trimethyldiphenylphosphine oxide (TMDPO) has been especially shown to be suitable for the initiation of photo-polymerization processes, wherein α-scission occurs in TMDPO to produce diphenylphosphinoyl (DPO) and 2,4,6-trimethylbenzoyl (TMB) radicals as fragments.[3] The DPO radical has been shown to react with vinyl compounds to form starting radicals ($i=1$ in $RM_i\cdot$, where $R\cdot$ and M denotes the DPO radical and vinyl monomer, respectively) by the time-resolved ESR spectroscopy.[3]



Scheme 1. The photo-initiated polymerization process of vinyl compounds, where i denotes number of monomer units in the growing chain.

The time-resolved cw-ESR is able to detect rapid reaction in photochemical systems and has been used as an excellent tool not only in assigning intermediate radicals based on their hyperfine interactions but also in investigating spin polarization processes. However, the spectrum, immediately after laser irradiation, is distorted suffering from the Torrey oscillation.[4] Moreover, finite microwave power, continuously applied during cw-ESR detection, often causes power-saturation phenomenon.

FT-ESR has recently been applied to investigate many photochemical systems such as the quenching of triplets by the quinone compounds.[5-8] The pulsed-ESR methodology, where microwave field is absent during detection, enables us to get the exact time profiles of ESR signals without any distortion. FT-ESR, however, has a difficulty in the assignment of widely spread ESR spectra due to the narrow range of excitation.

We applied the time-resolved cw- and FT-ESR spectroscopies complimentarily to investigate the photo-initiated polymerization of isoprene and MMA. TMDPO was purchased from Aldrich Chemical Co. and used without purification. Isoprene and MMA were purchased from Kanto Chemical Co. and were distilled under vacuum. Benzene of special pure grade was purchased from Kanto Chemical Co. TMDPO and monomers were dissolved in benzene and deoxygenated by bubbling the argon gas. The solution was circulated under continuous deoxygenation through a quartz flat-cell in an ESR cavity resonator. The sample was irradiated with the light pulse of a YAG-laser (Spectra Physics Co.), at 355 nm wavelength, 10mJ/pulse power, and 10Hz repetition rate.

In FT-ESR detection, the laser was externally triggered by a pulse generator in the pulsed-ESR apparatus (JEOL JES-PX1050). The free induction decay signal was generated by a microwave pulse of 20 ns duration and 1 kW power. In order to examine time profile of the FT-ESR spectra, the time interval between the

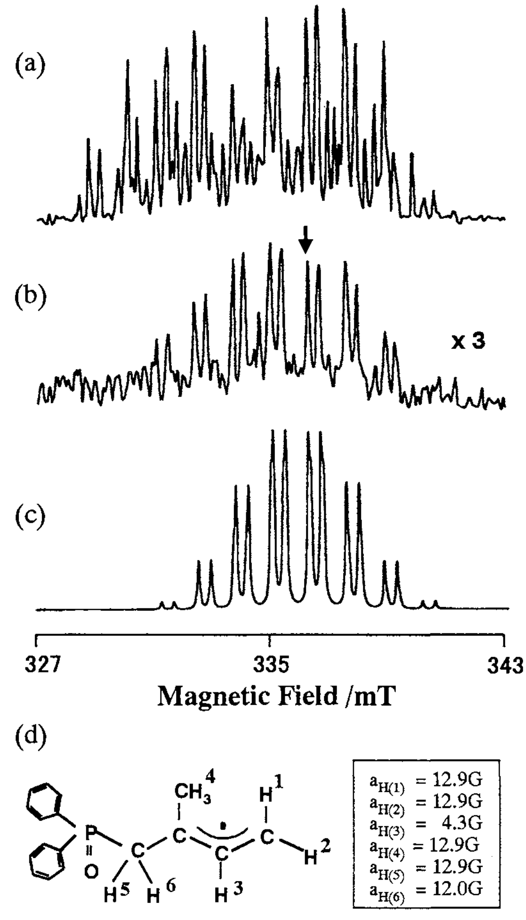


Figure 1. Time-resolved ESR spectra in isoprene obtained (a) 1 μs, (b) 5 μs, after laser irradiation. Simulated spectrum for (b) and the possible structure are shown in (c) and (d), respectively.

laser light and the microwave pulse was swept with an increment of 10 ns. The jitter of the laser was less than 1 ns. Phase-alternations of the microwave pulse and the quadrature detection were employed to eliminate the unwanted signals.

Figure 1 shows time-resolved cw-ESR signals obtained in the isoprene system after laser irradiation. The spectrum obtained 1 μs after laser irradiation showed a large hyperfine coupling of ca. 5.2 mT due to a phosphorous nucleus. (Figure 1a) The spectrum showed total absorption where population between spin states was largely polarized due to CIDEP effect. The large spin-polarization seemed to be transferred from that of the DPO radical. Kamachi et al. have assigned this spectrum to a starting radical in the propagating step of the radical polymerization of isoprene.[9] Turo et al. have obtained a similar kind of radical in the MMA system.[10] These results suggested that the rate of formation of the starting radical, k_1, was faster than the spin-lattice relaxation rate of the DPO radical, $1/T_1^{(0)}$, because spin-polarization of the DPO radical should be transferred to the starting radical before spin polarization of the DPO radical disappears. Although the primary propagating radical would be expected to be observed in the same manner since vinyl monomers would make chain reaction, there has been no direct report so far for detecting propagating radicals.

The spectrum obtained 5 μs after laser irradiation has no hyperfine coupling due to P nucleus. (Figure 1b) This spectrum was well reproduced by the spectral simulation shown in Figure 1c, where hyperfine couplings of only H nuclei were found in the spectrum. When the TMB radical adds to an isoprene monomer, similar spectral feature may be expected. However, it was assured that the spin-lattice relaxation time of the TMB radical was about 150 ns and so the polarization of the TMB radical should be extinguished before the radical in Figure 1b is formed. Therefore the ESR spectrum in Figure 1b could be attributed to the primary propagating radical (*i=2*) of isoprene. The estimated structure of the primary propagating radical (*i=2*) and hyperfine coupling constants (hfcc) used in the spectrum simulation are shown in Figure 1d. Since this set of hfcc is almost identical with that reported for the stationary isoprene radical generated by the continuous UV-irradiation,[9] the spin density of the unpaired electron on each H nucleus in the primary propagating radical was supposed to be similar to that of the growing radicals (*i*>>*2*). A similar primary propagating radical was also found in the MMA system.

To investigate reaction kinetics and spin-relaxation phenomenon for the radicals in the propagating process, the time-profile of the CIDEP signal was examined by FT-ESR spectroscopy. Figure 2 shows the time-dependence of the FT-ESR signal at the magnetic field positioned by an arrow in Figure 1b. In order to investigate time-dependence of the propagating radical, a linear differential equation, written as

$$d[\mathrm{RM}_i\cdot]/dt = \mathrm{k}_i[\mathrm{RM}_{i\text{-}1}\cdot][\mathrm{M}] - \mathrm{k}_{i+1}[\mathrm{RM}_i\cdot][\mathrm{M}] - \sum_n \mathrm{k}_t[\mathrm{RM}_i\cdot][\mathrm{RM}_n\cdot].$$

for the *i*-th stage of propagation, is to be solved numerically. The first term, the second term, and the third term correspond to the rate of formation, consumption, and bimolecular termination. Including the spin-lattice relaxation term, the intensity of CIDEP for the primary propagating radical, I_2, could be expressed by following equation where the asterisk denotes the spin-polarized molecule,

$$I_2 \propto d[\mathrm{RM}_2^*\cdot]/dt = \mathrm{k}_2[\mathrm{RM}^*\cdot][\mathrm{M}] - [\mathrm{RM}_2^*\cdot]/\mathrm{T}_1^{(2)},$$

when k_2 and $1/T_1^{(2)}$ are much larger than $k_3, \cdots, k_n$ and k_t. As plotted in Figure 2, the experimental profile was reproduced by use of appropriate parameters as listed in Table 1. It is noteworthy that the rate constant of the monomer addition to the growing radical chain drastically drops as the number of monomer unit in the chain increases (*i=0, 1,* and *n*).

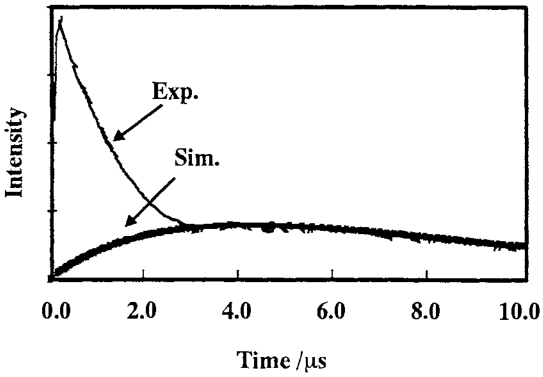


Figure 2. Time-profile of the FT-ESR signal at the magnetic field as pointed out by an arrow in Figure 1b. The result of simulation calculated with parameters in Table 1 is shown.

Table 1. Kinetic and spin-relaxation parameters obtained through numerical fitting to the time profile of the FT-ESR signal

	K_1 /10^8 $M^{-1}s^{-1}$	k_2 /10^4 $M^{-1}s^{-1}$	k_n /10^2 $M^{-1}s^{-1}$	$T_1^{(1)}$ /μs	$T_1^{(2)}$ /μs
MMA	1.3	22.0	1.87 [a]	1.8	4.5
Isoprene	1.1	1.0		2.1	4.5

[a] Kamachi et.al, *Adv.Polym.Sci.*, **38**, 55 (1981).

In conclusion, the primary propagating radical (*i=2*) in the photo-initiated polymerization process was observed in isoprene and MMA for the first time. The kinetic and the spin-lattice relaxation parameters were determined through quantitative approach to the time dependence of the FT-ESR signals.

References and Notes

1 P.Lechtken, I.Buethe, and A.Hesse, DOS 2830927 (1980) (BASF AG).
2 P.Lechtken, I.Buethe, M.Jacobi, and W.Trimborn, DOS 2909994 (1980) (BASF AG).
3 M.Kamachi and K.Kuwata, *J.Chem.Soc.,Perkin Trans.2*, **1988**, 961.
4 K.A.McLauchlan, in "Modern Pulsed and Continuous Wave Electron Spin Resonance," ed by L.Kevan and M.K.Bowman, Wiley, New York (1990), Chap.7, p.285.
5 T.Prisner, O.Dobbert, K.P.Dinse, and H. van Willigen, *J.Am.Chem.Soc.*, **110**, 1622 (1988).
6 M.K.Bowman, M.Toporowicz, J.R.Norris, T.J.Michalski, A.Angerhofer, and H.Levanon, *Isr.J.Chem.*, **28**, 215 (1988).
7 M.Pluschau, A.Zahl, K.P.Dinse, and H. van Willigen, *J.Chem.Phys.*, **90**, 3153 (1989).
8 A.Angerhofer, R.J.Massoth, and M.K.Bowman, *Isr.J.Chem.*, **28**, 227 (1988).
9 M.Kamachi, A.Kajiwara, K.Saegusa, and Y.Morishima, *Macromolecules*, **26**, 7369 (1993).
10 E.Karatekin, B.O'Saughnessy, and N.J.Turro, *Macromolecules*, **31**, 7992 (1998).