Time-Resolved Electron Spin Resonance Study on Radical Polymerization with (2,4,6-Trimethylbenzoyl)diphenylphosphine Oxide. Direct Estimation of Rate Constants for Addition Reactions of Diphenylphosphonyl Radicals to Vinyl Monomers

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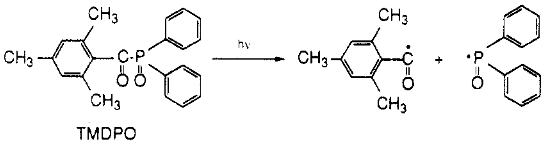
ABSTRACT: Rate constants for addition reactions of diphenylphosphonyl radicals ($Ph_2\dot{P}{=}O$) to vinyl monomers were directly estimated by time-resolved electron spin resonance (ESR) spectroscopy. The rate constants were on the order of 10^6–10^7 s^{-1} M^{-1}, being 1 or 2 orders of magnitude larger than those of carbon-centered radicals, which were obtained by photolysis of benzoin, benzoin methyl ether, or 1-phenyl-2-hydroxy-2-methylpropanone-1. The fact that (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMDPO) is a more effective initiator than α,α'-azobis(isobutyronitrile) (AIBN) was made clear in the radical polymerizations of vinyl pivalate at −30 and −70 °C.

Introduction

Acylphosphine oxides and acylphosphonates have received attention as a new type of photoinitiator for photocuring of polymer resins.[1-3] Schnabel et al.[4-7] performed laser photolysis of these compounds in the absence and presence of vinyl monomers and indicated that phosphorus-centered radicals formed by the photolysis of these compounds were much more reactive with vinyl monomers than carbon-centered radicals which were obtained by photolysis of benzoin, benzoin methyl ether, or 1-phenyl-2-hydroxy-2-methylpropanone-1. However, they had no direct evidence on the phosphorus-centered radicals. Accordingly, ESR study has been carried out for an understanding of the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMDPO).[8] The diphenylphosphonyl radical could not be detected by ESR measurements under continuous irradiation with a high-pressure mercury lamp, but the diphenylphosphonyl and 2,4,6-trimethylbenzoyl radicals (Scheme I) were detected as transient species by time-resolved ESR spectroscopy with laser pulse irradiation.[8] In the extension of the above studies on the photolysis of TMDPO, the lifetime of the diphenylphosphonyl radical was shown to decrease with increasing concentration of the vinyl monomers, while that of the 2,4,6-trimethylbenzoyl radical did not change in both the presence and absence of vinyl monomers in the time region of 4 μs after irradiation of 355-nm laser light.[9,10] This result shows that the diphenylphosphonyl radical is more reactive with vinyl monomers than the 2,4,6-trimethylbenzoyl radical and allows us to estimate rate constants for the addition of the diphenylphosphonyl radical to vinyl monomers.

In this study, we applied the time-resolved ESR spectroscopy combined with laser pulse irradiation to determine the rate constants for the addition reactions of the diphenylphosphonyl radical to various vinyl monomers and estimated directly the addition rate constants to monomers.

Scheme I



Experimental Section

TMDPO was provided by BASF and Nippon Kayaku Co., Ltd. TMDPO was purified by recrystallization from ethanol before use. Vinyl monomers commercially available were purified by distillation just before use. Radical polymerizations of vinyl pivalate was carried out with TMDPO or AIBN at −30 or −70 °C under irradiation with a high-pressure mercury lamp. A Pyrex glass ampule containing a monomer and an initiator was degassed, sealed under high vacuum, and irradiated for a given time. Polymers thus formed were purified by reprecipitation from tetrahydrofuran (THF)–methanol. The molecular weights of the polymers were measured by GPC (a Tosoh high-speed liquid chromatograph system, CCP&8010 series, equipped with RI and UV detectors using THF as an eluent) calibrated by standard polystyrene. 5-[4-(Acrylamido)phenyl]-10,15,20-triphenylporphyrin (acrylamide-TPP) was synthesized according to the previous paper.[11] A benzene solution of TMDPO (5.26 × 10^{-2} M) containing various concentrations of monomers was taken in a flat ESR sample cell. Laser pulses were irradiated by using a Q-switched Nd:YAG laser (Quantaray DCR-2) operated at the third harmonic (54 mJ/flash at 355 nm with a 6-ns fwhm). For the measurements of the time-resolved ESR, a JEOL JES-FE1X spectrometer was operated without magnetic field modulation, and the data were stored in an Iwatsu D901 transient memory at a sampling rate of 10 ns/word. Magnetic fields at resonance signals were determined by an Echo Electronics ES-FC5 NMR field meter. A block diagram of time-resolved ESR measurements is shown in Figure 1. The diphenylphosphonyl radicals generated by the laser pulse irradiation were observed at magnetic fields of 315.0 and 350.2 mT, whose separation corresponded to the hyperfine splitting constant of the diphenylphosphonyl radical with a phosphorus nucleus.[12] The decay of the ESR signals at 350.2 mT was recorded over a period of 40 μs after laser pulse irradiation.

Results and Discussion

Decays of ESR signals due to the diphenylphosphonyl radicals in the laser photolysis of TMDPO in the presence of varying concentrations of phenyl vinyl ether (PVE) are

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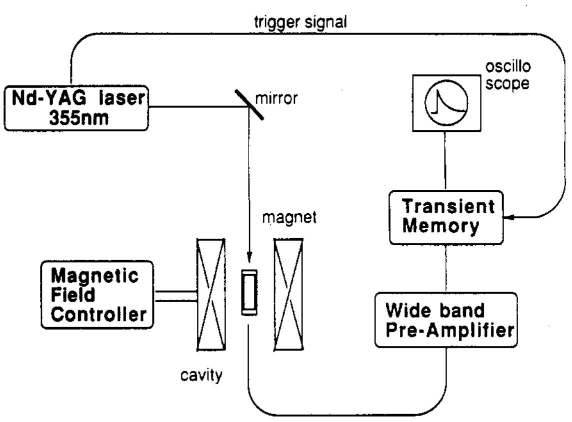


Figure 1. Schematic diagram of the system for time-resolved ESR spectroscopy.

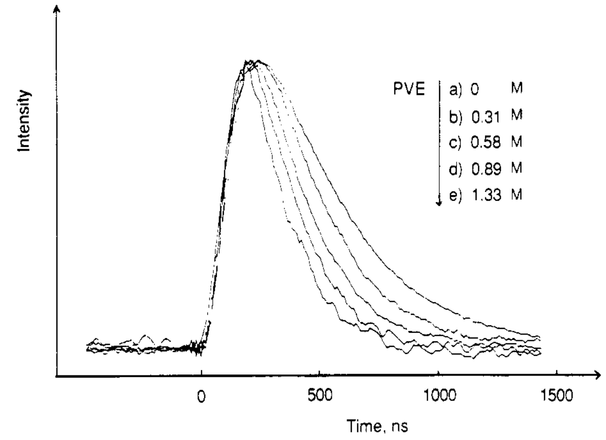


Figure 2. Time profiles of ESR signal intensities due to the diphenylphosphonyl radicals in the presence of varying concentrations of phenyl vinyl ether (PVE): (a) 0, (b) 0.31, (c) 0.58, (d) 0.89, and (e) 1.33 M.

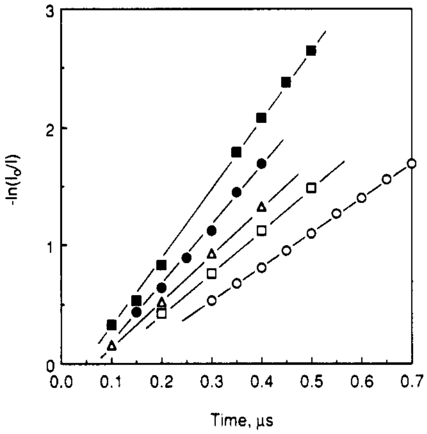


Figure 3. First-order plots for the decays of the diphenylphosphonyl radicals in the presence of varying concentrations of phenyl vinyl ether (PVE): 0 (○), 0.31 (□), 0.58 (△), 0.89 (●), and 1.33 M (■).

shown in Figure 2. The decays became faster with increasing concentration of PVE. The first-order plots for the signal intensities gave linear relationships in both the absence and presence of the monomers (Figure 3). The apparent first-order rate constant (k') increased with increasing monomer concentration. The plots of the k' value against the monomer concentration yielded linear relationships as shown in Figure 4. Accordingly, k' follows

$$k' = k_1 + k_2[\mathrm{M}]$$

where k_1 is the first-order decay constant in the absence of the monomer, and k_2 is the bimolecular rate constant for the reaction of the diphenylphosphonyl radical with the monomer. Similar results were observed in the time-resolved ESR measurements in the presence of 15 kinds of vinyl monomers. Their k_2 values are summarized in Table I.

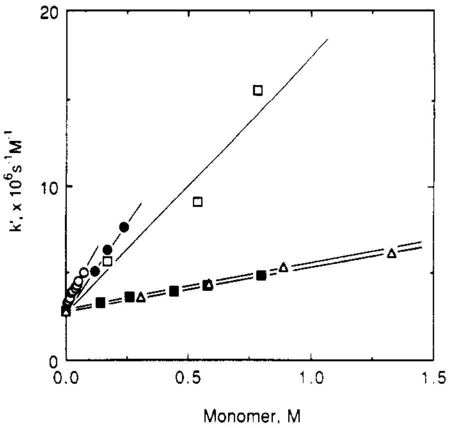
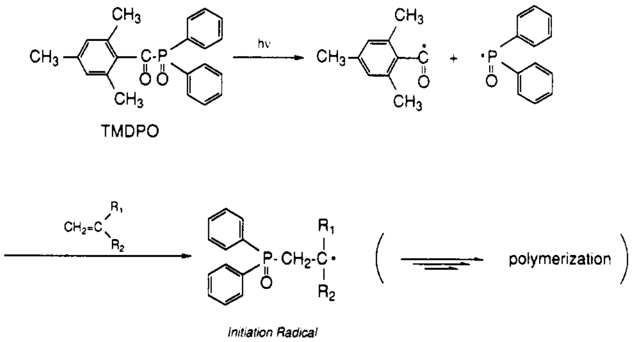


Figure 4. Plots of k' vs the concentration of added monomers: 1,1-diphenylethylene (○), di-n-butyl itaconate (●), 1-acetoxybutadiene (□), phenyl vinyl ether (△), and vinyl pivalate (■).

Table I
Rate Constants on Addition Reactions of the Diphenylphosphonyl Radical to Vinyl Monomers in Benzene at 20 °C

monomer	k_2, s^{-1} M^{-1}
1,1-diphenylethylene	$(2.4 \pm 0.2) \times 10^7$
di-n-butyl itaconate	$(1.9 \pm 0.1) \times 10^7$
N-methylacrylamide	$(1.6 \pm 0.2) \times 10^7$
methyl methacrylate (MMA)	$(1.6 \pm 0.4) \times 10^7$
1-acetoxybutadiene	$(1.5 \pm 0.2) \times 10^7$
α-methylstyrene	$(1.4 \pm 0.2) \times 10^7$
styrene	$(1.1 \pm 0.2) \times 10^7$
ethyl vinyl ether	$(1.5 \pm 0.3) \times 10^6$
n-butyl vinyl ether	$(4.4 \pm 0.3) \times 10^6$
i-butyl vinyl ether	$(2.5 \pm 0.2) \times 10^6$
n-decyl vinyl ether	$(3.1 \pm 0.2) \times 10^6$
phenyl vinyl ether	$(2.6 \pm 0.2) \times 10^6$
vinyl acetate	$(2.7 \pm 0.1) \times 10^6$
vinyl pivalate	$(2.5 \pm 0.1) \times 10^6$
acrylamide-TPP	$(1.6 \pm 0.3) \times 10^6$

Scheme II



The diphenylphosphonyl radicals decayed in the time region of 2 μs after irradiation, and new ESR signals appeared around the 2,4,6-trimethylbenzoyl radical at about 200 ns after irradiation.[9] The signals were reasonably assigned by computer simulation to a radical produced by the addition of the diphenylphosphonyl radical to methyl methacrylate (MMA) and α-methylstyrene. Therefore, k_2 is concluded to be the rate constant for the addition reaction of the diphenylphosphonyl radical to a vinyl monomer (Scheme II), which corresponds to the initiation rate constant in the radical polymerization of a vinyl monomer with TMDPO. These rate constants are on the order of 10^6–10^7 s^{-1} M^{-1}, which is 1 or 2 orders of magnitude larger than those of carbon-centered radicals, whose rate constants have been determined to be on the order of 10^4–10^5 s^{-1} M^{-1}.[5] The decays of the signals due to the 2,4,6-trimethylbenzoyl radicals, which were formed along with the diphenylphosphonyl radical by the photolysis of TMDPO, were identical over a period of 40 μs after irradiation in both the absence and presence of monomers, indicating that the 2,4,6-trimethylbenzoyl radicals did not attack vinyl monomers within this time region. This result shows that the 2,4,6-trimethylbenzoyl radical is less reactive with vinyl monomers than is the diphenylphosphonyl radical.

The rate constants for di-*n*-butyl itaconate, 1-acetoxybutadiene, MMA, and styrene derivatives, whose propagating radicals can be stabilized by delocalization of the radicals over substituents,[13] are on the order of 10^7 s^{-1} M^{-1}, while those for vinyl acetate, vinyl pivalate, and vinyl ethers, whose propagating radicals are difficult to conjugate with their substituents,[13] are on the order of 10^6 s^{-1} M^{-1}.

Among the styrene derivatives, the rate constants decreased in the order 1,1-diphenylethylene > α-methylstyrene > styrene. This can also be reasonably explained by resonance stabilization of the resulting radicals with the substituents: the radical resulting from 1,1-diphenylethylene is most stabilized by resonance with two phenyl groups, and that from α-methylstyrene is stabilized by hyperconjugation with a methyl group.

The rate constant of *N*-methylacrylamide was also on the order of 10^7 s^{-1} M^{-1}. This order of magnitude is reasonable because of the stabilization of the propagating radical by delocalization into a substituent. However, the rate constant of acrylamide having a tetraphenylporphyrin moiety (acrylamide-TPP) was 1 order of magnitude smaller than that of *N*-methylacrylamide. This difference is probably due to the steric hindrance of the bulky porphyrin moiety on the addition reaction of the diphenylphosphonyl radical.

In the series of vinyl ethers, the addition rate constants seem to be similar. These results show that the substituent does not influence the reactivity of the olefinic bond. Usually, vinyl esters such as vinyl acetate and vinyl pivalate are known to have higher radical reactivity than do vinyl ethers. However, the addition rate constants of the diphenylphosphonyl radical to vinyl ethers are almost the same as those in vinyl esters. This question still remains unanswered.

TMDPO seems to be a good initiator for the radical polymerization, because the diphenylphosphonyl radical is more reactive than a carbon-centered radical by 1 or 2 orders of magnitude. Accordingly, we performed the radical polymerizations of vinyl pivalate with TMDPO and AIBN at low temperatures. The results are shown in Table II. When we compare the results at −30 °C, the yields of poly(vinyl pivalate) initiated by TMDPO were considerably higher than those initiated by AIBN, while the molecular weights of the polymers were almost the same. These results show that the initiation occurs more effectively with TMDPO than with AIBN, being consistent with the fact that chemically induced dynamic electron spin polarization (CIDEP) of a 2-cyano-2-propyl radical is not influenced by MMA present.[14]

Table II
Radical Polymerizations of Vinyl Pivalate Initiated by TMDPO or AIBN

initiator	wt %	temp, °C	time, h	yield, %	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
TMDPO	0.1	−70	1	trace		
	0.1	−70	20	trace		
	0.5	−70	3	9.6	2.8×10^5	1.64
	0.1	−30	1	9.2	10.3×10^5	2.77
	0.1	−30	3	10.3	9.7×10^5	2.46
	0.5	−30	0.5	98.7	9.0×10^5	3.93
AIBN	0.1	−30	3	2.5	8.9×10^5	2.05
	1.0	−30	4	11.7	11.2×10^5	2.82

In conclusion, rate constants for the addition of the diphenylphosphonyl radical to vinyl monomers were directly estimated by time-resolved ESR spectroscopy with laser pulse irradiation and were found to be 1 or 2 orders of magnitude larger than those of carbon-centered radicals. In addition, it was made clear that TMDPO was a more effective initiator for radical polymerization below 0 °C than AIBN.

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