

## Chemical Intermediates in Radical Polymerization

### Measurement by Time Resolved ESR

The time-resolution of normal ESR is limited by modulation of the magnetic field. In order to measure short-lived radicals caused by laser-excitation, faster time-resolution is needed. An attachment to make such a measurement possible is the ES-CIDEP3 Time Resolved ESR (TR-ESR). By direct observation of radicals whose spin system is polarized by Chemically Induced Dynamic Electron Polarization (CIDEP) caused by photo-cleavage, a time-resolution as short as 200ns is possible.

The composition of the instrument is shown in Fig. 1. The laser pulse excites the sample inside the resonator (C in Fig. 1), and the signal from intermediates is amplified by a wide band preamplifier, and accumulated in a digital oscilloscope. The data is recorded along a time axis and stored in a PC.

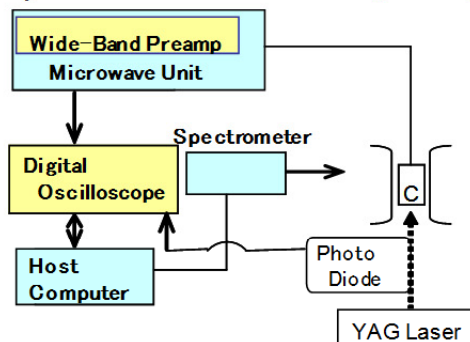


Photo-Diode and Laser should be user provision

Fig.1 Composition of Time Resolved ESR

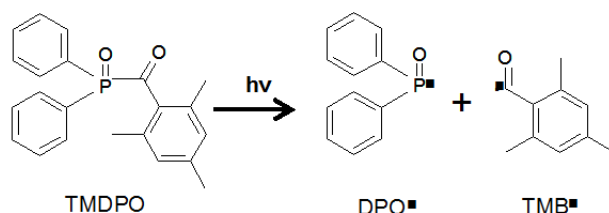


Fig. 2 Laser Cleavage Reaction of TMDPO

Fig. 3 shows a time axis spectrum of DPO (Fig. 2) caused by laser photo-excitation (355nm) of a benzene solution of 2,4,6-Trimethylbenzoyl diphenylphosphineoxide (TMDPO). It shows that an intermediate radical is created in a very short time, but decays due to rapid spin-lattice relaxation. After obtaining a set of time-axis spectra recorded with varying magnetic fields, the ESR signal can be plotted against the magnetic field. (Fig. 4) Since field modulation is not applied, absorption signals composed of 2 lines due to P-nuclei (DPO) and 1 line from TMB are measured.

If monomer is present in this system, it is possible to monitor ESR signals derived from the propagating radicals directly. As shown, TR-ESR can be a useful tool for observing chemical intermediates.

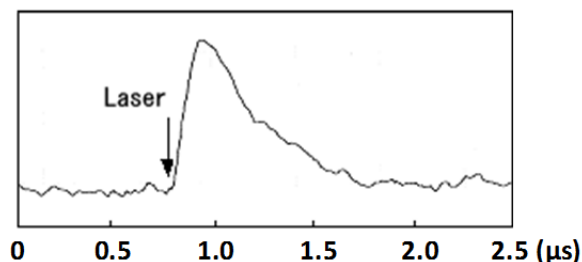


Fig. 3 ESR Signal of DPO• vs. time

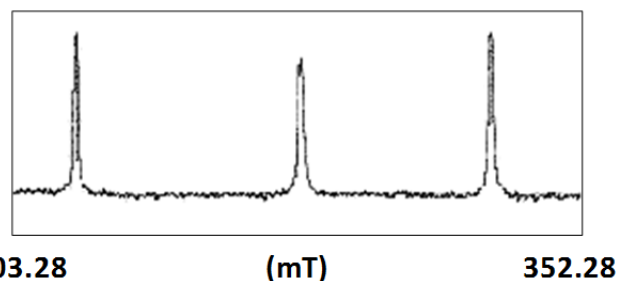


Fig.4 TR-ESR of radicals by photo-cleavage of TMDPO.

Reference: Kamachi M. et.al, J. Chem. Soc. Perkin Trans. II **1988**, 961-965