

Measurement of Polymer Intermediates by Time Resolved ESR II

Time Resolved ESR (CIDEP3 - TR-ESR) can measure short-lived radicals that arise from the very early stages of photochemical reactions with ~ 200 ns time resolution. (Refer to Application note : ER-090004).

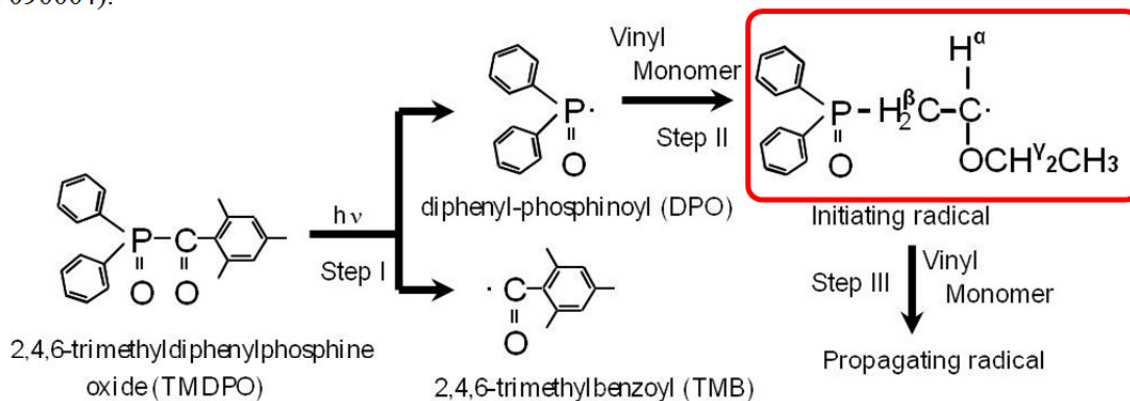


Fig. 1 Radical Polymerization Scheme Initiated by Photochemical Reaction

Fig.1 shows the radical polymerization reaction of vinyl monomer using TMDPO as polymerization initiator. As DPO^{\cdot} arising from laser decomposition of TMDPO has a very high reactivity, addition reaction proceeds with the monomer.

The starting radical, arising during the initial polymerization process using ethylvinylether as monomer, was measured by CIDEP3 and the result is shown in Fig. 2.

The spectrum when the intensity of the starting radical grows and decays in a very short time scale has been observed. The time resolved ESR spectrum just $2\mu\text{s}$ after laser irradiation is shown in Fig. 3. The hfs parameters, ($a_{\text{P}} = 6.77$ mT, $a_{\text{H}^{\alpha}} = 1.48$ mT, $a_{\text{H}^{\beta}} = 1.56$ mT, $a_{\text{H}^{\gamma}} = 0.18$ mT) correspond well with the structure of the starting radical.

As noted above, TR-ESR can be a very useful tool for analysing the reaction in photochemical processes.

Reference :

Y. Mizuta et.al. Appl. Magn. Reson. 19, 93-110 (2000)

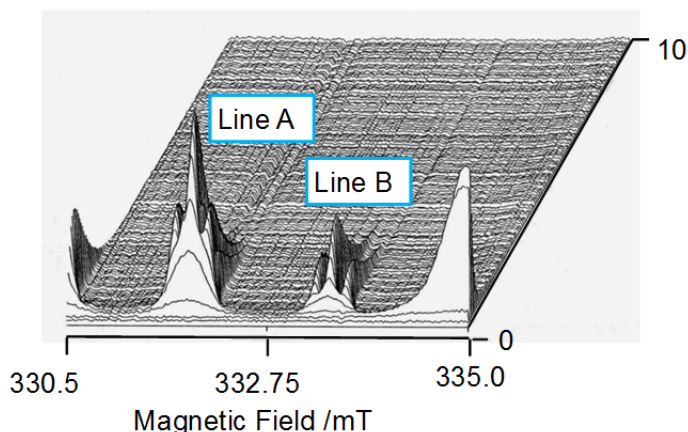


Fig.2 2D Spectrum of Starting Radical of Ethylvinylether

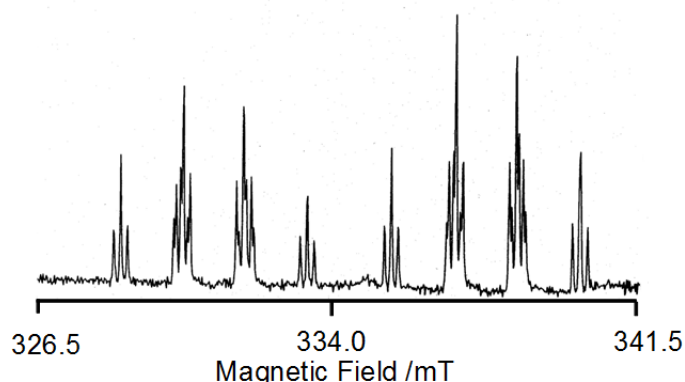


Fig.3 Spectrum of Starting Radical of Ethylvinylether