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Plenary Lecture

Time-resolved FT-ESR and CW-ESR Studies on Photo-initiated Polymerization

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Radical polymerization of vinyl monomers as initiated by the diphenylphosphinoyl (DPO) radical which is formed by the photo-cleavage of 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TMDPO) was investigated by cw-ESR and FT-ESR. Well resolved hfs's of the starting radicals were observed by the time-resolved of formation and the spin-lattice relaxation were determined by time-resolved FT-ESR for these starting radicals. In the polymerization of MMA and isoprene the primary propagating radicals were found for the first time by the observation of their well resolved hfs's using time-resolved cw-ESR. Based on the kinetic analysis including the spin-lattice relaxation, the rates of formation and the spin-lattice relaxation were determined by simulation of the time profile of FT-ESR for the primary propagation radicals of MMA and isoprene. The rate of the primary propagation step was found to be by two orders greater than an average value of whole propagation steps as obtained by a steady state measurement.