AN ESR STUDY OF THE INFLUENCE OF THE PRESENCE OF LITHIUM SALTS ON THE PHOTOINICIATED RADICAL POLYMERIZATION OF METHACRYLIC MONOMERS

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The photoinitiated bulk free radical polymerization of alkyl methacrylate momers in the presence or absence lithium salts was studied at different lithium salt concentrations and using 2-2-dimetoxi-2-phenyl-acetophenone (IRG) as photoinitiator, at room temperature. The polymerization process was monitored by electron spin resonance (ESR) technique. The reaction mixtures, introduced in quartz tubes of 3 mm inner diameter and placed in the resonant cavity of the ESR spectrometer , were irradiated with a 175 W Xenon lamp at wavelengths in the range between 250-400 nm, where free radicals are produced as a consequence of the homolytic rupture of the photoinitiator. The propagating radicals formed were recorded with a Bruker ESP 300 spectrometer and the conditions to register the spectra were: microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 3G; conversion time, 40 ms; time constant, 655 ms; sweep time, 42s; power, 6.32 mW; receiver gain 3×10^5; scan number, 5.

Propagating radical concentrations at different reaction time were estimated by double integration of the ESR signals and comparison with that obtained for known concentrations of 2,2,6,6-tetramethyl-4-hydroxylpiperidine-1-oxyl (TEMPOL), used as standard.

The ESR spectra of the propagating radicals showed a typical 13-line spectral pattern characteristic of the methacrylic radicals in a fluid medium. By using different reaction conditions, the polymerisation kinetics of the different monomer/Li^+ mixtures were studied and the experimental results were interpreted by considering the influence of the lithium cation, as complexing agent, on the bimolecular radical termination rate constants.

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