FREE-RADICAL-INDUCED CHAIN SCISSION AND CROSS-LINKING OF POLYMERS IN AQUEOUS SOLUTION – AN OVERVIEW

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In the radiolysis of N_2O-saturated aqueous solutions •OH are generated. In their reactions with polymers, they give rise to polymer-derived radicals. The kinetics of the formation and decay of these radicals are reviewed. The rate of reaction of a polymer with a reactive free radical is noticeably lower than that of an equivalent concentration of monomer due to the non-random distribution of the reaction sites. Once a larger number of radicals are formed on one polymer molecule, e.g. upon pulse radiolysis, close-by radicals recombine more rapidly while the more distant ones survive for much longer times than an equivalent concentration of freely diffusing radicals. Intermolecular cross-linking (between two polymer chains, increase in molecular weight) and intramolecular cross-linking (formation of small loops, no increase in polymer weight) are competing processes, and their relative yields thus depend on the dose rate and polymer concentration. Hydrogen-transfer reactions within the polymer, e.g. transformation of a secondary radical into a tertiary one, are common and facilitated by the high local density of reactive sites. Due to repulsive forces, the lifetime of radicals of charged polymers is substantially increased. This enables even relatively slow b-fragmentation reactions to become of importance. In the case of poly(methacrylic acid), where β-fragmentation is comparatively fast, this even leads to an unzipping, and as a consequence of the efficient release of methacrylic acid the situation of equilibrium polymerization is approached. Heterolytic β-fragmentation is possible when adequate leaving groups are available, e.g. in polynucleotides and DNA. In the presence of O_2, chain scission occurs *via* oxyl radicals as intermediates. Some implications for technical applications are discussed.