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FREE RADICAL TRANSFER IN POLYMERS

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For the present study of free-radical transfer in polymers pulse radiolysis and product studies have been carried out in aqueous solutions using thus far only the water-soluble polymers polyacrylic acid, polymethacrylic acid and polyvinyl alcohol. When OH radicals, generated in the radiolysis of N₂O-saturated aqueous solutions, react with polymers the lifetime of the polymer radical thus created very much depends on the number of radicals per polymer chain. When there are a large number of radicals per chain their bimolecular decay may be faster than the corresponding (diffusion controlled) decay of monomeric radicals, but when the macromolecule contains only few or even just one radical their lifetime is considerably prolonged. Highly charged polymers such as polyacrylic acid at high pH attain a rod-like conformation which again favors a long lifetime of the radicals. Under such conditions, radical transfer reactions can occur. For example, in polyacrylic acid OH radicals generate two kinds of radicals side by side. The radical in β -position to the carboxylate group converts into the thermodynamically more stable α -radicals by an H-transfer reaction as can be followed by spectrophotometry. Besides radical transfer reactions β -fragmentation reactions occur causing chain scission. Such reactions can be followed in a pulse radiolysis experiment by conductometry, because counter ions are released upon chain scission. Such a process is especially effective in the case of polymethacrylic acid, where it results in a chain depolymerization.

An intramolecular H-abstraction is also observed in the γ -radiolysis of polyacrylic acid with the corresponding peroxy radicals. This causes a chain reaction to occur. The resulting hydroperoxides are unstable and decarboxylate given rise to acetylacetone-like products. In polyvinyl alcohol the peroxy radicals in α -position to the alcohol function undergo HO₂-elimination. This prevents a scission of the polymer chain in the bimolecular decay of the peroxy radicals. However, at the high dose rate of E-beam irradiation the bimolecular decay of the peroxy radicals becomes so fast that it competes effectively with the HO₂-elimination and thus causes considerable chain scission.