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“Application of radiation methods to study kinetics of radical reactions in aqueous solutions of monomers and polymers”

ABSTRACT

Fast development of many industrial sectors, especially those that use advanced technologies, contributes to the need for new functional polymers whose structure is designed to achieve pre-established specific features and functions of polymeric materials to serve, in a dedicated way, various advanced applications. To achieve that, new methods of synthesizing polymers having controlled structure and properties have been developed and are constantly being improved, including techniques based on controlled radical polymerization. This requires precise knowledge on the kinetics and mechanism of radical polymerization and crosslinking reactions.

This work was related to the kinetics of radical reactions in polymer systems. It was undertaken to investigate such issues as the kinetics of radicals reactions with macromolecules and kinetics of intermolecular recombination radicals of polymer in dilute solutions, as well as to develop and test a new method of determining the rate constants of propagation in radical polymerization.

The first problem was to investigate the kinetics of diffusion-controlled reaction of small radicals (i.e. radicals located on the low-molecular-weight molecules) with model macromolecules. As a small radical and polymer model, the hydroxyl radical $\cdot\text{OH}$ and poly(*N*-vinylpyrrolidone) - PVP were selected, respectively. Studies were performed for PVP standards of various molecular weights. Physicochemical parameters of PVP standards, such as molecular weight, radius of gyration and hydrodynamic radius were determined experimentally by multi-angle laser light scattering. Rate constants of the reaction of $\cdot\text{OH}$ radicals with PVP standards have been measured by pulse radiolysis using the standard competition technique. The influence of chain length and polymer concentration on the rate constant was studied in detail. It was shown, that the rate constant values of the studied reaction increase with increasing polymer concentration, which in combination with data from the literature confirmed that this effect is a general feature of small-radical reactions with macromolecules. It was noted, that for a constant, low polymer concentration (lower than the

critical hydrodynamic concentration) the rate constant is related to the macromolecule size. It was found, when comparing reaction radius calculated from Smoluchowski equation on the basis of experimental data with physicochemical parameters of the macromolecules, that a good approximation of the reaction radius of macromolecules, in their diffusion-controlled reactions with small substrates in dilute solution, is the radius of gyration.

The next issue was the intermolecular recombination kinetics of polymer radicals. The study consisted of generating, by short pulses of high-energy electrons, single radicals on macromolecules of the same length, and then tracking their rate of recombination based on the changes in absorbance at times from nano- to milliseconds. The model system was recombination of poly(*N*-vinylpyrrolidone) radicals in dilute, deoxygenated aqueous solution. Reaction conditions (polymer concentration lower than critical hydrodynamic concentration and range of electron pulse dose from 20 to 80 Gy) were chosen in a such way that individual chains, that form coils in solution, were separated from each other and the average number of radicals generated on each chain was lower than 1. Then the obtained kinetic runs were analyzed and assessed by fitting with various kinetic models. It was found that the decay of polymer radicals by intermolecular recombination in dilute solutions cannot be well fit using a simple, homogeneous, second-order kinetics. Much better fit was obtained with the Płonka model (dispersive kinetics) or by assuming a combination of two second-order reactions. The best fit was obtained using the latter model, for which the rate constants of the faster and the slower reaction were determined. It was found that the fraction of the rapid process is not strongly dependent on the initial concentration of radicals, and decreases with increasing chain length. It was suggested that the fast reaction is spatially associated with the surface of the coil and the slower one with radicals "buried" inside the coil (the larger the coil, the lower probability of the radical to be found at or near the surface). It is noted that both, faster and slower, reaction rate constant dependence on the chain length is of a similar nature. The values of the obtained rate constants are significantly lower than predicted by the model assuming that the rate of reaction is controlled by translational diffusion of the coils. It was therefore considered that the decisive process governing the kinetics of intermolecular recombination polymer radicals in dilute solutions is segmental diffusion, or relative movement of the segments of the macromolecule.

In the final part of the work a new method for determination of propagation rate coefficient in radical polymerization using pulse radiolysis was proposed and tested. The method, based on subjecting monomer solution to a series of fast electrons pulses and subsequent

chromatographic analysis of products, was called PEP-SEC (*Pulsed Electron Polymerization - Size Exclusion Chromatography*). *N*-vinylpyrrolidone was chosen as a model monomer. The polymerization was carried out in aqueous solution at room temperature. As a first step, polymerization conditions were established (dose per pulse 0.25 Gy, total short irradiation time – 1 minute and the radiation pulse frequency 20 Hz). Radical polymerization was carried out for different monomer concentrations and the formed polymer chains were analyzed by gel permeation chromatography (GPC). Based on the molecular weight distribution results and applying formula used in the PLP-SEC method (this method uses pulses of laser light to initiate polymerization), the propagation rate coefficient was calculated. It was shown, that the proposed method works well and leads to correct results, which are in good agreement with literature data. It was noted, that result obtained using PEP-SEC method not only reproduce well the individual values of propagation rate coefficient determined by the standard PLP-SEC technique but also follow the PLP-SEC data in demonstrating the tendency of change with monomer concentration. In both cases the rate coefficient values decrease with monomer concentration. The main advantages of the new method in comparison to the already well developed PLP-SEC are: no need for using photo-initiators and – in the future – possibility of application to non-transparent systems.

It was shown that radiation techniques are a valuable tool for conducting research in the field of kinetics and mechanism of radical reactions in polymer systems.

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