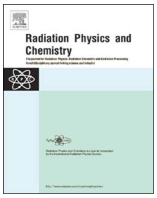
Radiation Physics and Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Novel system for pulse radiolysis with multi-angle light scattering detection (PR-MALLS) – concept, construction and first tests

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ARTICLE INFO

Keywords:
Pulse radiolysis
Laser light scattering
Degradation
Polymerization
Cross-linking

ABSTRACT

Time-resolved pulse radiolysis, utilizing short pulses of high-energy electrons from accelerators, is an effective method for rapidly generating free radicals and other transient species in solution. Combined with fast time-resolved spectroscopic detection (typically in the ultraviolet/visible/near-infrared), it is invaluable for monitoring the reactivity of species subjected to radiolysis on timescales ranging from picoseconds to seconds. When used for polymer solutions, pulse radiolysis can be coupled with light-scattering detection, creating a powerful tool for kinetic and mechanistic analysis of processes like degradation or cross-linking of macromolecules. Changes in the light scattering intensity (LSI) of polymer solutions are indicative of alterations in the molecular weight and/or in the radius of gyration, i.e., the dimensions and shape of the macromolecules. In addition to other detection methods, LSI technique provides a convenient tool to study radiation-induced alterations in macromolecules as a function of time after the pulse. Pulse radiolysis systems employing this detection mode have been so far constructed to follow light scattered at a single angle (typically the right angle) to the incident light beam. Here we present an advanced pulse radiolysis & multi-angle light-scattering-intensity system (PR-MALLS) that has been built at IARC and is currently in the phase of optimization and testing. Idea of its design and operation is described and preliminary results for radiation-induced degradation of pullulan as well as polymerization and crosslinking of poly(ethylene glycol) diacrylate are presented. Implementation of the proposed system provides a novel research tool, which is expected to contribute to the expansion of knowledge on free-radical reactions in monomer- and polymer solutions, by delivering precise kinetic data on changes in molecular weight and size, and thus allowing to formulate or verify reaction mechanisms. The proposed method is universal and can be applied for studying both natural and synthetic polymers. The developed system can be also valuable in studies of the border of biology and medicine, especially on radical reactions of biopolymers and their conformational transitions. Furthermore, capability to follow fast changes in mass and dimensions of nanobjects may be of significant importance for nanoscience and nanotechnology.

1. Introduction

Pulse radiolysis (Kroh, 1986; Ebert et al., 1965; Tabata, 1991) is a method of initiating and study fast reactions that relies on subjecting the sample to a short pulse of ionizing radiation (usually accelerated electrons) and studying the triggered chemical reactions or physical processes. This allows for identification of short-lived intermediates, analysis of reaction kinetics on microsecond (or shorter) time scale and, in consequence, determination of reaction mechanism Spectrophotometric detection, the most frequently used analyzing method in pulse radiolysis, is based on recording changes in absorbance occurring in the irradiated system during and after the pulse of ionizing radiation. It provides the possibility of recording spectra of the short-lived reaction intermediates and following kinetics of their formation and decay. In case of polymer radiolysis (where in general the micro- and millisecond time scales are used) important questions center around the kinetics and mechanism of cross-linking or degradation processes, while for polymerization processes the possibility of determining the rate constants of elementary reactions such as propagation are of fundamental importance. However, pulse measurements with spectrophotometric detection very often turns out to be not suitable for following these reactions. For instance, when following the chain scission process, spectrum of the product (a terminal polymer radical generated at the end of the chain fragment) is typically very similar to the spectrum of the substrate (a mid-chain radical before the chain break). In such cases, spectrophotometric detection is not selective enough and cannot

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http://dx.doi.org/10.1016/j.radphyschem.2017.04.010
Received 28 October 2016; Received in revised form 29 March 2017; Accepted 14 April 2017

Please cite this article as: Kadlubowski, S., Radiation Physics and Chemistry (2017), http://dx.doi.org/10.1016/j.radphyschem.2017.04.010

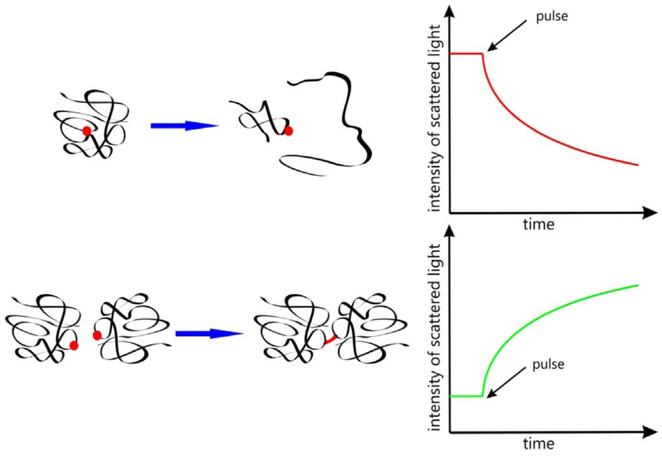

Fig. 1. Changes in the intensity of scattered light after a pulse of ionizing radiation for chain scission and intramolecular cross-linking.

be applied to follow the reactions in question (Kujawa et al., 1998).

The above-mentioned problems can be solved by time-resolved analysis of intensity of scattered light after the pulse (Beck et al., 1974; Tabata, 1991). The essence of the measurement can be explained as follows (Fig. 1): if the result of irradiation is a main chain scission, new, shorter polymeric chains are formed. Since the average molecular weight of the polymer is decreased, accordingly a decrease in the intensity of the light scattered by the solution is observed. Changes in the signal recorded as a function of time can be used to calculate the kinetic parameters of reaction (reaction order, rate constant) as well as amplitude-related parameters as the radiation yield of chain scission. One should take into consideration that the observed changes in light scattering intensity in a polymer system undergoing degradation can reflect one (or both) of two processes – the real chemical reaction of chain breakage, or the physical process of separation of the newly formed chain fragments, depending on which of them is slower. Experimental protocols allow to differentiate between these two phenomena. Similar reasoning can be applied for the process of intermolecular cross-linking. In this case increase of intensity of light scattered by polymer solution after the pulse of ionizing radiation is observed.

The physics of light scattering allows to directly correlate the angular dependence of scattered light intensity with the size of the scattering entity (a macromolecule, a nanoparticle, etc.). Therefore, application of simultaneous time-resolved measurement of intensity of light scattered at many angles should provide a unique possibility of following the fast changes in molecular size, independently of the measurements of the molecular weight (i.e., the chain length). Moreover, since the theory of light scattering requires extrapolation to zero angle when calculating the molecular weight from scattered light intensities, having the possibility of simultaneous multi-angle measurements should largely improve the accuracy of molecular weight determination in comparison to single-angle measurements, where extrapolation is not possible and re-calculation based on (often poorly known) scattering functions are necessary (Kratochvil, 1987).

While the free-radical generation method in a polymer system employing a pulse of ionizing radiation, being very convenient and clean (no initiators), is not the most common one, further steps of free-radical reactions are identical with processes initiated by other free-radical-generation methods (as thermal decomposition of initiators, photochemistry, sonochemistry, etc.). Therefore the proposed experimental method and setup are of broad, universal application and may be used for studying kinetics and mechanism of most kinds of free-radical-induced reactions in polymer solutions.

To the best of our knowledge, so far only three systems for pulse radiolysis with light scattering detection have been built worldwide. All these setups allowed for collecting the scattered light only at a single angle. The systems constructed at the Hahn-Meitner-Institut für Kernforschung in Berlin and at the Institute of Applied Radiation Chemistry, Lodz University of Technology, were based on collecting the scattered light at right angle to the incident laser beam (Tabata, 1991) and the other one (Max-Planck-Institut für Strahlenchemie, Mülheim an der Ruhr) allowed to collect the scattering light at a very low angle of ca. 5° (Low-Angle Laser Light Scattering - LALLS) (Deeble et al., 1990; Ulanski et al., 1996).

Notwithstanding the inherent limitations of the single-angle approach (see below), these systems have yielded many valuable results, vital to our current understanding of kinetics and mechanisms of radical-induced reactions in polymer solutions (Beck et al., 1975, 1977; Lindenau et al., 1977; Grollmann and Schnabel, 1980; Horie and Schnabel, 1984; Rosiak and Schnabel, 1984; Schnabel, 1986; Deeble et al., 1990; Rosiak et al., 1990; Debble et al., 1991; Al-Assaff et al., 1995; Ulanski et al., 1996; Janik and Rosiak, 2002).

The light scattering detection method also proved very useful in studies on radiation-induced chain scission and cross-linking in nucleic acids (Lindenau et al., 1976a, 1976b; Bertincharnps, 1978; Washino and Schnabel, 1980, 1982a, 1982b, 1982c; Washino et al., 1983, 1984; Denk and Schnabel, 1982; Denk et al., 1983; Melvin et al., 1996).

The unique advantage of light scattering detection coupled with pulse radiolysis has been presented by Kujawa and et al. (1998). First attempt has been made to observe on-line polymerization process, i.e., polymerization of N-vinylpyrolidone (VP) in aqueous solution.

However, pulse radiolysis with single-angle light-scattering detection has some drawbacks. It does not allow to distinguish between the processes of degradation or cross-linking and conformational changes such as shrinkage of coil or intramolecular cross-linking, i.e., they do not allow for independent size determination, and also that the molecular weight values were rather estimated than calculated, due to lack of possibility to extrapolate the light scattering results to zero angle.

In order to overcome the above-mentioned limitations of single-angle light scattering detection, we have developed a concept of a new type of system for measurement of the intensity of scattered light coupled to pulse radiolysis, which differs from the previously applied solutions in simultaneous multi-angle detection of scattered light. The new design will give a possibility of direct measurements of changes in the radius of gyration independently from the changes of molecular weight. At the same time it will increase the accuracy of molecular weight measurement and will allow following reactions related to changes in conformation including intramolecular cross-linking (synthesis of micro- and nanogels).

2. Experimental

Pullulan standard, a product of Shodex, of nominal weight-average molecular weight 853 kDa, and poly(ethylene glycol) diacrylate (PEGDA), a product of Sigma-Aldrich, of nominal number-average molecular weight 700 Da, were used as received. Solutions (2.5 mg/ml and 20 mg/ml, respectively) were made up with ultrapure water (Milipore MiliQ) at least 24 h before use. Before irradiation PEGDA solutions have been saturated with argon to remove oxygen.

Pulse irradiation (see discussion in the text below) with an electron beam was performed using an ELU-6 linear accelerator (Eksma, Russia) delivering pulses of 6 MeV electrons of pulse duration 4 μs (dose per pulse of ca. 400 Gy as determined by alanine dosimetry (eScan, Bruker)).

3. Results

3.1. PR-MALLS construction

Main goal of the work was the design and construction of novel