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Determination of Propagation Rate Coefficient for the Polymerization of *N*-Vinylpyrrolidone in Aqueous Solution by Pulsed Electron Polymerization and Size Exclusion Chromatography

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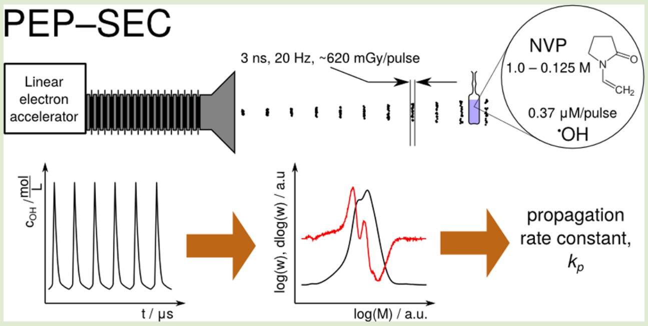
ABSTRACT: A new method for determination of a propagation rate coefficient in radical polymerization, pulsed electron polymerization–size exclusion chromatography (PEP–SEC), has been tested on *N*-vinylpyrrolidone in water and shown to yield results very similar to those obtained by the well-established pulsed laser polymerization–size exclusion chromatography (PLP–SEC). A potential advantage of PEP–SEC is its applicability to studying polymerizations in nontransparent systems and lack of any additives. Series of nanosecond pulses of high-energy electrons from an accelerator generate radicals which initiate polymerization. Further analysis of the samples and data processing are the same as in PLP–SEC. The described technique can be potentially developed into a method complementary and/or comparative to PLP–SEC.



More than 50% of polymer production worldwide is based on radical polymerization.[1] New perspectives in this field have been opened with the advent of controlled radical polymerization processes.[1−5] The key prerequisite for rational and successful use of these methods for synthesizing well-defined polymers of predefined molecular weight and structure is detailed knowledge on the reaction mechanism and kinetics. Within the last two decades great progress has been made in precise determination of propagation rate coefficients, using the IUPAC-recognized method of pulsed laser polymerization–size exclusion chromatography (PLP–SEC). This method is very well established, both theoretically and in practice, with hundreds of papers published and excellent reviews being available.[6−15]

While PLP–SEC is very universal, it has at least two disadvantages. It is not suitable for systems of limited transparency of laser light, and it requires the presence of a photoinitiator, which in some cases might interfere with the studied reactions. An alternative analogous method, free of these two limitations, has been proposed relatively early in the development of PLP–SEC[16] but never actually extensively tested. This method is based on using series of short pulses of fast electrons instead of pulses of laser light. High-energy electrons, being a form of ionizing radiation, lead to formation of monomer radicals, thus initiating polymerization.[17−23] No initiator is needed, and the polymerizing system does not need to be transparent.

Electron accelerators are less frequently found in research laboratories than lasers. However, there are well-established experimental techniques, such as pulse radiolysis,[24,25] which utilize pulsed accelerators that are suitable for PEP–SEC without major adjustments. As to the monomer range, the method is expected to be quite universal. Ionizing radiation can induce ionization and subsequent radical formation in almost any organic matter, including monomers, while, depending on the studied system, the dominating mechanism of initiation and the radical yield can vary.[22,24−27] In aqueous solutions the indirect mechanism dominates, involving energy absorption by solvent and subsequent reactivity transfer to monomer (see below), while for many organic solvents the solvent-assisted pathway may be less effective and monomer radicals can be generated mainly by direct absorption of ionizing radiation by monomer molecules. Radical yield is expected to be relatively low in monomers and solvents bearing aromatic groups, due to effective dissipation of energy. This can be compensated by using higher doses of ionizing radiation per pulse. The doses can be easily adjusted, so that the concentration of generated radicals can be precisely controlled. Maximum radical concentrations achievable in electron pulse systems similar to the one used in this work are in the order of 0.1−1 mmol/dm^3, which is much higher than actually needed for the discussed kinetic experiments.

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It should be mentioned that determination of a propagation rate coefficient in a heterogeneous system using PEP−SEC requires the knowledge of monomer concentration in the monomer-bearing phase. When monomer is contained only in one well-defined phase, its concentration can be easily calculated or measured. In other cases partition coefficients must be known, while in still more complex systems local monomer concentrations may vary due to phenomena of adsorption/absorption, electrostatic interactions, aggregation, etc. Here the use of PEP−SEC must be combined with other experimental techniques and calculation models. Furthermore, determination of molecular weight distribution after polymerization in a heterogeneous system will require separating the polymer from other components. On the other hand, as demonstrated by van Herk et al.,[16] PEP−SEC itself can potentially be used to determine the monomer concentration in the polymer-bearing phase of a nontransparent system, if the value of propagation rate coefficient is known.

While the cited pioneering work of van Herk et al.[16] has demonstrated the feasibility of using electron pulses for determination of propagation rate coefficients, the results of that work could not be compared to analogous data obtained by classical methods, simply because the chosen complex, nontransparent system (polymerization of styrene in polystyrene latex) could not be assessed by the well-established techniques. The aim of this work is to demonstrate the reliability of the PEP−SEC approach as an alternative to PLP−SEC, by performing measurements on a polymerizing system which has been recently studied in detail by the well-established PLP−SEC technique and comparing the obtained results. Results presented below concern the propagation rate coefficient of radical polymerization of *N*-vinylpyrrolidone (VP) in water at 22 °C. These data are compared to the results of a recent detailed PLP−SEC study on the same system.[28]

In experiments described in this study, deoxygenated aqueous solutions of VP have been subjected to a series of short pulses of high-energy electrons. During each pulse, the dominating process in the studied system was radiolysis of water, leading to the formation of hydroxyl radicals, hydrogen atoms, and hydrated electrons (reaction 1).[24,29] Hydrated electrons, which in most cases do not initiate polymerization, can be easily instantaneously converted to further $^\bullet$OH radicals by saturating the solution with nitrous oxide (reaction 2).[30] $^\bullet$OH radicals and H$^\bullet$ atoms initiate polymerization by addition to the monomer double bond, thus forming the monomer radical (reaction 3), typically a very fast, diffusion-controlled reaction.[31−34] While reaction with $^\bullet$OH and H$^\bullet$ was the main initiation pathway in the conditions of our study (so-called indirect effect), some initiation by direct effect, i.e., direct energy absorption by monomer molecules leading to monomer radical formation, was also taking place, but its contribution to the monomer radical yield was never higher than 10%.

$$H_2O \rightarrow e_{aq}^-, {}^\bullet OH, H^\bullet, H_2O_2, H_2, H^+, OH^- \quad (1)$$

$$N_2O + e_{aq}^- + H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \quad (2)$$

$$^\bullet OH(H^\bullet) + M \rightarrow HO{-}M^\bullet(H{-}M^\bullet) \quad (3)$$

For indirect effect, the radiation yield *G* (defined as quantity of radicals generated by absorbing 1 J of energy) of $^\bullet$OH and H$^\bullet$ radicals in N_2O-saturated solutions is well-known ($G = 6 \times 10^{-7}$ mol/J).[30] Basing calculations on indirect effect only, the used dose corresponds to 0.37 μmol/dm^3 of radicals generated per each pulse in our system.

Growing polymer chains initiated by the first electron pulse have undergone termination by recombination with radicals generated during the second, third, and further pulses. In this way, similarly as in the PLP−SEC, distinct populations of chains have been formed of the length resulting from propagation periods between two, three, etc. electron pulses. These chain lengths were subsequently assessed by SEC. Analyses of molecular weight distributions by the latter method were performed directly on the irradiated samples, without monomer separation. In test measurements on model poly(*N*-vinylpyrrolidone) (PVP) samples of similar molecular weight as in samples resulting from irradiation experiments, addition of up to 1 M of monomer (which was well separated from the polymer on the SEC columns) did not noticeably alter the MW distribution results. Exemplary SEC results are shown in Figure 1, as the molecular weight distribution and its first derivative.

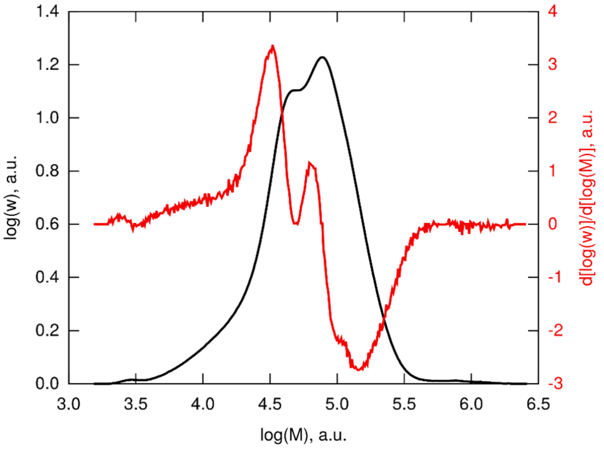

Figure 1. Molecular weight distribution of PVP and its first derivative obtained in PEP−SEC experiment at monomer concentration of 0.5 M.

It can be noticed that in the first-derivative curve three deflection points can be distinguished. The first and second of them have been taken for calculations.

Irradiation at each particular set of conditions was performed 3 times, and the resulting deflection point locations (in terms of the corresponding chain lengths) were averaged. Analysis of the location of the first and second deflection point on the derivative curve of MW distribution led to the chain length formed during one and two periods between the pulses, respectively. By applying formula 4 used in the PLP−SEC technique

$$L_i = i \times k_p \times [M] \times t_p \quad (4)$$

where *L* is the chain length (degree of polymerization); *i* is the number of periods between pulses during which the chain was growing (here $i = 1$ or 2); k_p (in dm^3 mol^{-1} s^{-1}) is the propagation rate coefficient; [M] (in mol dm^{-3}) is the monomer concentration; and t_p (in s) is the time between the pulses, based on the SEC results, the k_p values can be calculated.

For each analyzed sample we could calculate the values of k_p corresponding to the chains having grown during one and two periods between the pulses. As expected, both k_p values thus obtained were very similar (the ratio of molecular weights corresponding to the first and second deflection points, M1/M2, was in the range 0.50−0.57, which satisfies one of the IUPAC recommendations set for PLP−SEC). These values were subsequently averaged. To compensate monomer depletion, for each condition a series of experiments were run at various total number of pulses (from 200 to 1800), and the resulting rate coefficient values were extrapolated to zero pulses. The so-obtained final k_p values are presented in Figure 2. Our results obtained for experiments performed at various monomer concentrations are presented in parallel to the literature data of Stach et al.[28] obtained by PLP−SEC at 25 °C.

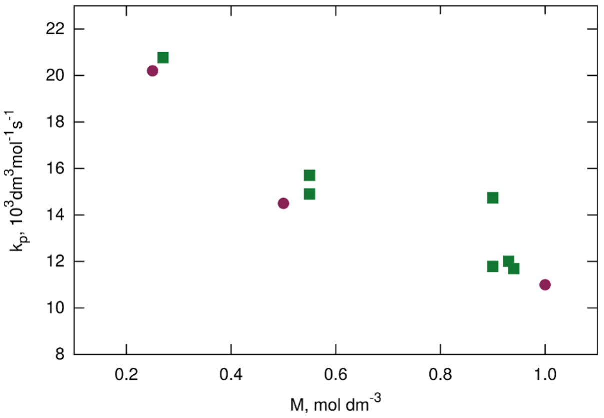

Figure 2. Comparison between k_p values obtained during PEP−SEC as determined at 22 °C (red circles) and PLP−SEC experiments at 25 °C (green squares). PLP−SEC data from Stach et al. (2008).[28]

No adjustment of our data to 25 °C was made in Figure 2 since, taking into account the relevant activation energy of 16.0 ± 1.4 kJ/mol,[28] the correction would amount to ca. 0.7% of the measured value, i.e., definitely lower than the experimental error.

We can see that the results obtained using the electron-pulse-based 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 the rate coefficient value to decrease with monomer concentration. While we cannot exclude that the observed dependence is to some extent influenced by the band broadening effect in SEC due to different final polymer concentration, such dependencies of k_p on [M] have been evidenced and analyzed in detail before not only for *N*-vinylpyrrolidone[28,35] but also for nonionized methacrylic acid[36] and *N*-vinylformamide,[35,37] and they are believed to be real effects caused mainly by weakening of intermolecular interactions between VP molecules, leading to an increase of rotational mobility in the transition state structure for propagation.

An issue which may require a comment regarding the accuracy of PEP−SEC is the occurrence of side reactions induced by radiation. For instance, in aqueous solutions $^\bullet$OH and H$^\bullet$ radicals can react not only with monomer and with terminal radicals at the growing polymer chains but also by abstracting hydrogen atoms from random positions along the newly formed macromolecules. These midchain radicals could initiate chain breakage, cross-linking, and branching and thus influence the GPC results. However, we do not expect these side effects to be of higher importance than the side reactions, such as chain branching, accompanying PLP−SEC studies.[38−41] It has been demonstrated in many works for simple hydrophilic vinyl monomers that reactivity of the main products of water radiolysis with monomer molecules is much higher than with monomer units along a polymer chain (a factor of 20 in terms of rate constants is not uncommon).[31−34,42,43] Taking into consideration that PEP−SEC, as PLP−SEC, is operated at relatively low monomer conversion; i.e., the concentration of monomer units in the newly formed polymer chains is much lower than that of monomer molecules; the probability of an $^\bullet$OH radical to abstract a hydrogen atom from a random site along a macromolecule is low; and we do not expect a significant influence of cross-linking, branching, and degradation on the molecular weight distributions. Nevertheless, the probability of side reactions in PEP−SEC should be definitely carefully studied in the further development of PEP−SEC, including viscometric technique, NMR, and multiangle static light scattering.[44,45]

While the described experimental system and procedures may still need to be optimized, and its full compliance with the strict rules defined for PLP−SEC has yet to be demonstrated, we believe that the presented results prove the utility and accuracy of the PEP−SEC technique as an alternative and/or comparative method to the well-established PLP−SEC. We believe that it may be of particular use when studying polymerizations in nontransparent systems or in cases where the photoinitiator used in PLP−SEC is expected to interfere with the propagation process.

■ EXPERIMENTAL SECTION

N-Vinylpyrrolidone (Fluka) (VP) was purified by distillation. VP solutions were made up in water purified by Millipore Milli-Q system (TOC < 4 ppm, 0.5 μm filtered, specific resistivity 18.2 MΩ cm). Solutions were saturated with oxygen-free nitrous oxide and irradiated at 22 °C in gas-tight glass vessels by a series of pulses of fast electrons from a linear electron accelerator[46] (ELU-6, Eksma, Russia, for details see ref 47). Pulse duration was 3 ns, pulse frequency 20 Hz, and electron energy 6 MeV, i.e., of sufficient penetration to provide relatively uniform energy deposition in the whole irradiated volume. Dose per pulse was 0.62 Gy (1 Gy = 1 J/kg), as determined by alanine dosimetry.[48] Series of up to 1800 pulses were used. Irradiated samples were directly injected (100 μL) into the SEC setup consisting of P580 pump (Dionex), two Polymer Laboratories Aquagel−OH MIXED 8 μm columns operated at 30 °C, and a triple detector system (Viscotek RALLS detector, Viscotek Dual Detector Refractometer/Viscometer model 250, λ = 670 nm). The triple detection systems allow for molecular weight distribution measurements without prior molecular weight calibration on polymer standards. Water was used as the eluent at a flow rate of 1.0 mL/min (refractive index n = 1.330 at 30 °C, λ = 670 nm[49]). Determination of instrument parameters (detector offsets, etc.) was performed on a single narrow PEO standard of a molecular weight in the range expected for PVP resulting from our experiments (78 kDa, Polymer Laboratories, dn/dc = 0.133).[50] Final checking was made using broad PVP standards (4.3−360 kDa, American Polymer Standards). Obtained values of M_w were within 15% of the nominal ones. The dn/dc value of PVP in water was taken as 0.185 cm^3 g^{-1}.[50] A TriSEC GPC Software GPC-Viscometry Module, version 3.0, was used for data analysis.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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