PhD Thesis-books

Pulse Radiolysis of Acrylic Acid Ester and Acryamide Type Monomers in Dilute Aqueous and Cyclohexane Solutions

By

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I. Backgroud

The high-energy radiation initiated polymerization of the acrylamide derivatives is an industrially applied method. However, the kinetics of the underlaying reactions were rarely investigated, and the scattered results are contraversal. We know very little form the literature about the important reactions such as the first reaction steps (initiation) between the monomer and the intermediates formed in the radiolysis of the solvent. In this dissertation the reaction mechanism of the radiation initiated reactions were analysed by identifying the intermediate structures, the buildup and the decay kinetics. The study was extended to molecules with similar chemical structure and considering the available data in the literature also the statements were generalized. As a result of the comprehensive research work the physico-chemical and reaction-kinetical interpretation of the processes initiated by accelerated electrons were achieved and also data from the literature were critically discussed.

II. Summary of The Applied Experimental Methods

The reactions of the vinyl type monomers were studied in their dilute aqueous and cyclohexane solutions by pulse radiolysis method. The measurements were mostly carried out with the pulse radiolysis setup applying the 4 MeV Linac electron accelerator with kinetic spectrophotometric detection of the Institute of the Isotope and Surface Chemistry (HAS) and also with a 12 MeV Linac type pulse radiolysis equipment of the ISOF (CNR) in Bologna. The pulse radiolysis measurements made with kinetic spectrophotometric detection were completed with conventional UV-VIS spectrophotometric measurements.

During the experiments made in aqueous solutions the hydrated electron, H atom and OH radical intermediates formed in the water radiolysis react with the solute monomer. In cyclohexane solutions the cyclohexyl radicals initiate the reactions.

III. New Scientific Results

1. In the reaction of acrylamides the **hydrated electron** formed in the water radiolysis adds to the carbonyl group.

    (The rate coefficient of the reaction is close to the so-called diffusion controlled rate coefficients, $\sim 10^{10}$ mol^{-1} dm^{3} s^{-1}.)

2. The short lived electron adduct has two absorption bands, one with high and one with 5 times lower intensity.

    (For acrylamide monomers the more intensive band is located at 270-300 nm, the less intensive appears at ~400 nm, while in the case of acrylic acid esters there is only one maximum between 270 and 290 nm.)

3. The wavelength of the absorbance maximum belonging to the more intensive peak changes with the pH of the solution due to the reversible protonation of the electron adduct intermediate.

    (In acidic solutions the protonated radical form exists, while in alkaline solution the non protonated radical anion is observed. The wavelength difference between the absorption maxima of the protonated and the ionic intermediates was 10-30 nm.)

4. The equilibrium constants of the reversible protonation were calculated by a new exact method. The negative logarithm of the constant for acrylamides is high (pK_a 8-10), for acrylic acid esters medium values were measured (5-7), while for dialkil fumatates and maleates pK_a is small (3-5).

(Signodial titration-type curves were measured by varying the pH of the solution.)

5. The equilibrium constant of the reversible protonation is mainly determined by the rate coefficients of the deprotonation.

   (Using the Hammett σ_p values the role of the substituent groups were studied. Electron withdrawing groups resulted in moderate deprotonation rate coefficients by stabilizing the protonated radical form. The electron acceptor groups had opposite effect.)

6. Irreversible protonation was also observed on the β-carbon atom of the electron adduct.

   (An α-carboxyalkyl type radical is the product of the irreversible protonation.)

7. The **H atoms** add to the C=C double bond of the monomers studied.

   (The H atom adds to the β-carbon atom of the monomer and in the reaction an α-carboxyalkyl type radical forms.)

8. In solutions containing *tert*-butanol the H atoms react not only with the monomer, but also with the *tert*-butanol and the reaction rates are comparable.

   (In radiation chemistry of aqueous solutions the H atom reactions are studied in acidic solutions containing *tert*-butanol.)

   The separation of the rate coefficients of these reactions was carried out by applying the Stern-Volmer equation.

9. The rate coefficients for H atom reactions are in a very narrow range and their values are mainly determined by the reaction enthalpy.

   (In contrast to the general observations on the radical addition, the measured bimolecular rate coefficients for H atom reactions vary in a relatively narrow range from 2×10^{9} to 1.1×10^{10} mol^{-1} dm^{3} s^{-1}.)

   The R^1, R^2 and R^3 substituents of the $R^1HC{=}CR^2{-}C(O)R^3$ structure effectively modify the rate coefficient values of the H atom addition by changing the reaction enthalpy.

10. The **OH radical** adducts (formed directly in the reaction of the OH radical and the acrylamides) are α–carboxylalkyl type radicals. The absorbtion maxima of the OH adducts are at longer wavelengths for acrylamide type monomers than for the radicals formed in similar reactions of the acrylic acid esters.

    (The rate coefficient values are in the range of $0.73\text{-}1.2\times10^{10}$ mol^{-1} dm^{3} s^{-1} similarly to the rate coefficients of the hydrated electron reactions.)

11. With the increasing number of the alkyl substitution on the N atom of the monomer there is a shift of the maximum of the transient absorption to longer wavelengths.

    (In the OH adduct the unpaired electron can be conjugated with the O atom and the NH_2 group and the alkil substitution extends the conjugation.)

12. In alkaline solution the β OH derivative of the monomer formed by disproportionation is deprotonated.

    (In dilute solutions the decay is by disproportion or recombination.)

    The deprotonated form has a significant and intensive absorption band around 280 nm.

13. In concentrated solutions the decay of the primer radicals formed by OH addition takes place not only in self-termination. The probability of the radical-monomer reactions is high.

    (Due to the formation of dimer and greater radicals the reciprocal radical concentration as a function of time showed deviation from the linearity.)

14. In **cyclohexane** solutions in the contrast to other studies the polymerization of the studied monomers was found to follow radical mechanism.
15. The reactivity of the acrylic acid ester type monomers in the radical polymerization is significantly higher than in the case of methacrylates.
    (This result is in agreement with the literature.)
16. The termination rate coefficients of the oligomer radicals are approximately 1 order of magnitude smaller than the values found for monomer radicals.
17. The solvent influences the value of the termination rate coefficients.
    (The value of the termination rate coefficient is smaller in cyclohexane solutions than in aqueous solution.)
18. A linear relationship was found between the polymerization rate and the number of the carbon atoms in the ester chain. Similar tendency was not found for methacrylates.
    (In the case of acrylates for longer side chain greater propagation rate coefficient was found, while the value of the termination rate coefficient was reduced because of the increased radical size.)
19. By increasing the monomer concentration or with extending the time scale of detection the absorption maximum of the transient shifts to the longer wavelengths.

IV. Publications connected with the subject of the dissertation

1. Takács E., Dajka K., Wojnárovits L., Emmi S.S.: Protonation kinetics of acrylate radical anions. *Phys. Chem. Chem. Phys*., **2**, 1431-1433, 2000.

2. Takács E., Wojnárovits L., Dajka K.: Kinetics of the early stages of high-energy radiation initiated polymerization. *Macromol. Chem. Phys.*, **201**, 2170-2175, 2000.

3. Wojnarovits L., Takacs E., Dajka K., D′Angelantonio M., Emmi S.S.: Pulse radiolysis of acrylamide derivatives in dilute aqueous solution. *Radiat. Phys. Chem.*, **60**, 337-343, 2001.

4. Wojnárovits L., Takács E., Dajka K.**,** Emmi S.S.: On the reversible protonation of acrylic-type compounds. *Chem. Res. Intermed*., **27**, 847-854, 2001.

5. Takács E., Dajka K., Wojnárovits L.: Study of high-energy radiation initiated polymerization of butyl acrylate. *Radiat. Phys. Chem*., **63**, 41-44, 2002.

6. Takács E., Dajka K., Wojnárovits L., Emmi S.S.: Pulse radiolysis study of the initial steps of the polymerization of cyclohexyl acrylate and cyclohexyl methacrylate. *Radiat. Phys. Chem.*, **63**, 485-488, 2002.

7. Dajka K.: Akrilátok impulzusradiolízise ciklohexános oldatban. *Magy. Kém. Foly*., **108**, 325-328, 2002.

8. Wojnárovits L., Takács E., Dajka K., Russo M., D'Angelantonio M., Emmi S.S.: Rate coefficient of H atom addition to acrylate type olefins in aqueous solution. *Tetrahedron*, **59**, 8353-8358, 2003.

9. Wojnárovits L., Takács E., Dajka K., Emmi S.S., Russo M., D'Angelantonio M.: Re-evaluation of the rate coefficient for the H atom reaction with *tert*-butanol in aqueous solution. *Radiat. Phys. Chem*., **69**, 217-219, 2004.

V. Conference lectures on the subject of dissertation

1. Takács E., Wojnárovits L., Dajka K.: Radiolysis of the dilute aqueous solutions of acrylamide type monomers. *XXIInd Chemical Presentations Days,* Szeged 1-3. November 1999.

2. Wojnárovits L., Takács E., Dajka K.: Pulse radiolysis of acrylamide derivatives in dilute aqueous solution. *International Symposium on Prospects for Application of Radiation Towards the 21st Century,* Yokyo, Japan 13-17 March 2000.

3. Dajka K.: Radiolysis of the dilute aqueous solutions of acrylamide type monomers. *'Doki 3' Chemical School for PhD Students,* Chemical Research Center, HAS, Mátraháza 10-12 April 2000.

4. Takács E., Wojnárovits L., Dajka K.: Kinetic study of the high-energy initiated polymerization by pulse radiolysis. *Scientific Days of the Chemical Research Center*, CRC, HAS, Budapest 25-26 May 2000.

5. Takács E., Dajka K., Wojnárovits L.: On the protonation of the acrylamide and acrylic acid ester types of radical anions. *Radiochemical Days in Autum 2000,* Hévíz 18-20 October 2000.

6. Takács E., Wojnárovits L., Dajka K.: On the first steps of the high-energy initiated polymerization in cyclohexane solutions studied by pulse radiolysis**.** XXIIIrd *Chemical Presentations Days***,** Szeged 20-22 November 2000.

7. Dajka K., Takács E., Wojnárovits L.: On the high-energy initiated free radical polymerization of the acrylates in dilute cyclohexane solutions. *'Doki 4' Chemical School for PhD Students.* CRC, HAS, Mátraháza 20-22 May 2001.

8. Dajka K., Takács E., Wojnárovits L.: On the pulse radiolysis of the acrylates in cyclohexane solutions. *Radiochemical Days in Autum 2001,* Mátraháza 17-19 October 2001.

9. Dajka K., Takács E., Wojnárovits L.: On the pulse radiolysis of the acrylamides and acrylates. *Scientific Days of the Chemical Research Center*, CRC, HAS, Budapest 28-29 May 2003.

VI. Posters on the subject of the dissertation

1. Takács E., Dajka K., Wojnárovits L.: Study of High-Energy Initiated Polymerization of Butylacrylate. *1st International Conference on Polymer MoDification, DeGradation and StAbilisation (MoDeSt 2000),* Palermo, Italy 3-7 September, 2000.

2. Wojnárovits L., Dajka K., Takács E.: Pulse Radiolytic Investigation of Acrylate Polymerization in Aqueous Solution. Protonation of Electron Adducts. *6th International Meeting on Pulse Investigations in Chemistry, Biology and Physics. (Puls' 2000)* Łeba, Poland 9-15 September, 2000.

3. Takács E., Dajka K., Wojnárovits L. Emmi S.S.: Pulse radiolysis study of the initial steps of the polymerization of cyclohexyl acrylate. *12th International Meeting on Radiation Processing* Avignon, France 25-30 March, 2001.

4. Dajka K.: On the reaction of the H atom with conjugated double bonded aliphatic compounds. Pulse radiolysis experiments. *23rd Miller Conference on Radiation Chemistry and PULS'2003 Session*. Bialowieza, Poland 6-12 September, 2003.

VII. Scientific visits connected with the theme of dissertation

CNR Istituto per la Sintesi Organica e la Fotoreattività, Bologna, Italy
Pulse radiolysis study of acrylic and acrylamide type molecules in dilute aqueous solution.
Supervisor: S. S. Emmi

1. 21 September - 24 November 2002.
2. 12-23 May 2003.

VIII. Papers not related to the subject of the thesis

1. Dajka K., Takács E., Solpan D., Wojnárovits L., Güven O.: On the reaction of the C.I. Reactive Black 5 with the intermediates of water radiolysis. *10th Tihany Symposium on Radiation Chemistry*. Sopron 31 August - 5 September 2002.

2. Solpan D., Güven O., Takács E., Wojnárovits L., Dajka K.: High energy treatment of dye containing wastewater: steady state gama radiolysis experiments. *10th Tihany Symposium on Radiation Chemistry*. Sopron 31 August - 5 September 2002.

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4. Dilek S., Güven O., Takács E., Wojnárovits L., Dajka K.: High-energy irradiation treatment of aqueous solutions of azo dyes: Steady state gamma radiolysis experiments. *Radiat. Phys. Chem.*, **67**, 531-534, 2003.