1 Abstract

Rate coefficients of propagation, k_p, of termination, k_t, and of intramolecular transfer-to-polymer, k_{bb}, have been studied via pulsed-laser polymerization (PLP) methods for systems with strong intermolecular interactions, such as hydrogen bonds, and for polymerizations with two types of distinctly different radicals being present.

The propagation kinetics of methacrylic acid (MAA) and *N*-vinyl pyrrolidone (NVP) in aqueous solution has been investigated by the PLP-SEC technique which combines PLP-initiation with subsequent analysis of the produced polymer by size-exclusion chromatography. The experimental conditions of monomer concentration, temperature, pressure and degree of monomer ionization have been varied in wide ranges. The dependence of k_p on monomer-to-polymer conversion has been determined from PLP-SEC experiments with pre-mixed polymer. The variation of k_p may be adequately explained by the interaction of solvent and monomer molecules with the transition state structure for propagation. The termination rate coefficients of MAA and NVP have been studied by the SP-PLP-NIR method in which the change in monomer concentration after single pulse (SP) initiation is monitored via µs time-resolved near infrared spectroscopy (NIR). The variations of k_t with conversion for different initial monomer concentrations reflect the diffusion-controlled character of the termination step with k_t being governed by segmental, translational, and reaction diffusion.

In acrylate polymerization backbiting reactions may occur by which chain-end secondary propagating radicals (SPR) are transformed into tertiary midchain radicals (MCR) via 1,5-hydrogen shift. MCRs can react back to SPRs by monomer addition. The basic kinetic scheme has to be extended for additional reactions steps, as SPR and MCR species show widely different k_p and k_t, respectively. The impact of MCR formation on the applicability of the experimental techniques for k_p and k_t determination, i.e. PLP-SEC and SP-PLP-NIR, was investigated by PREDICI simulations. A novel experimental method has been developed by which k_{bb} and the rate coefficient for monomer addition to the MCR, k_p^t, for butyl acrylate (BA) have been determined from PLP-SEC experiments carried out under extended variation of laser pulse repetition rates. Insights into the kinetics, especially of the termination reactivity of secondary and tertiary acrylate radicals, have been obtained by measurements of full electron spin resonance (ESR) spectra under stationary UV and pseudo-stationary PLP initiation, respectively, or by time-resolved monitoring of SPR and MCR concentrations after application of a laser single pulse (SP-PLP-ESR). By the latter technique also chain-length-dependent individual k_t values are accessible.

For acrylic acid (AA) polymerization in aqueous solution, the complexities associated with strong solvent effects on the rate coefficients and with the pronounced MCR build-up add to each other. Attempts were made to consider the resulting consequences for the kinetic data of AA polymerization in aqueous solution published so far.

2 Introduction

Synthetic polymers are extensively used in almost all technical fields today with applications ranging from simple packaging material over furniture, clothes and automotive parts to high-tech devices, e.g. for aerospace engineering and life sciences. This widespread distribution makes modern life hardly imaginable without polymeric materials. Synthetic polymers stand out due to their versatile and tunable physical properties and their inexpensive and raw material saving production.

The age of commercial synthetic polymers started about 100 years ago by the work of Baekeland,[1] however it were the pioneering investigations of Staudinger[2,3] that form the basis of the scientific fields of polymer chemistry and polymer physics; he discovered the macromolecular chain structure consisting of chemically bonded monomeric units. Since those early studies, polymer production grew rapidly and is nowadays one of the major fields in chemical industry with a turnover in 2006 of about 26 bn € in Germany alone.[4]

Polymers may be synthesized via polycondensation, catalytic, ionic or free-radical polymerization (FRP). FRP is a robust and versatile technique which is employed to produce e.g. poly(ethylene), poly(styrene), poly(acrylates), poly(methacrylates), and corresponding copolymers as high-volume commodities. In conventional FRP the average lifetime of a growing chain is typically below 1 s which makes it impossible to actively intervene during chain growth. In controlled radical polymerization the lifetime of macroradicals is increased to hours, days or even longer by suppression of irreversible radical termination reactions. Since the breakthrough of such techniques in the 1990s, designing macromolecular architecture by radical polymerization has become possible providing easy access to e.g. blockcopolymers, star polymers and comb polymers.[5]

The physical properties of polymeric materials are in principle governed by the composition and microstructure of each single macromolecule within the ensemble of chains which form the bulk material. Parameters describing such ensembles of macromolecules, beside others, are the molecular weight distribution (MWD) and mean values, e.g., of the degree of short- or long-chain branching. The microstructure of a macromolecule is established during the polymerization process and is hence a result of the kinetics of the individual reaction steps which occur during chain growth. To allow for strategic and rational design of new materials, which is of great academic and industrial interest, two types of information are required: (*i*) the relation of microstructure and physical properties and (*ii*) the polymerization mechanism together with the associated reaction rates.

Estimation of polymer structure has become feasible in the last decade via sophisticated simulation programs by which not only the time-dependent change in concentration of the reacting species but also full MWDs, branching levels and (copolymer) composition of the formed polymer may be calculated. This development strengthens the need for accurate mechanistic models and rate coefficients. However, due to the mostly rather complex polymerization scheme these rate coefficients are not easily determined and are often not known with sufficient accuracy to allow for satisfactory simulation results. To resolve these problems, an IUPAC working party on "Modeling of Polymerization Kinetics and Processes" has been founded which addresses existing dilemmas and collates benchmark values, mostly for the propagation rate coefficient so far.[6–15]

The reaction rate in FRP is essentially governed by the rates of initiation, propagation, and termination. The propagation reaction is chemically controlled up to high monomer-to-polymer conversions.[16] The magnitude of the propagation rate coefficient, k_p, is determined by the properties of the transition state structure (TS) for propagation and its interactions with the solvent environment.[17–21] Thus, pronounced solvent effects on k_p are expected for systems in which strong, but different, monomer – monomer and monomer – solvent interactions occur. The termination reaction is assumed to be diffusion controlled from low conversions on which introduces an enormous complexity toward the description of this reaction step, as the corresponding rate coefficient, k_t, may change dramatically with monomer-to-polymer conversion, X, which is associated with an increase in solution viscosity. Moreover, k_t may depend on radical chain length, i, on macroradical mobility, on the location of the radical within the chain, on the MWD of the background polymer matrix and on solvent content and quality. Theoretical models have been proposed which are based on the physical understanding of the diffusion-controlled nature of the termination step and adequately describe the variation of k_t with X[22,23] and with i[24–27]. These models, however, cannot be used to predict k_t for unknown polymerization systems without some additional experimental data.

Classical methods for investigations into the individual rate coefficients of propagation and termination require the combination of results from experiments with stationary and instationary radical concentration yielding the coupled parameters k_t/k_p^2 and k_t/k_p, respectively. Application of such techniques may however pose problems in cases where the radical chain length distributions significantly differ in both experiments[7] or side reactions such as transfer-to-polymer[28] occur. The situation has been largely improved by the development of pulsed-laser polymerization (PLP) techniques about 20 years ago in which chain growth is induced by application of short laser pulses to reaction mixtures containing a photoinitiator. The propagation rate coefficient can be determined precisely by the PLP-SEC method, put forward by Olaj and co-workers,[29,30] in which PLP is combined with subsequent analysis of the formed polymer by size-exclusion chromatography (SEC). The variation of the termination rate coefficient with conversion is accessible by the SP-PLP-NIR technique, introduced by Buback et al.,[31] in which the change in monomer concentration after single pulse (SP) initiation is monitored via μs time-resolved near infrared (NIR) spectroscopy. Recently a novel technique was designed in which k_t is determined by direct tracing of radical concentrations after SP initiation using time-resolved electron spin resonance spectroscopy (ESR).[32] This SP-PLP-ESR technique provides direct access to chain-length dependent k_t values in conventional FRP.[32–34] However, the decrease of k_t toward increasing chain length may also be detected by SP-PLP-NIR applied to systems in which macroradical chain length is controllled by the addition of a reversible addition fragmentation transfer (RAFT)[35,36] agent.[37–39] Application of SP-PLP-NIR represents a significanty improvement compared to the so-called RAFT-CLD-T technique[40] in which k_t is determined from classical chemically induced polymerizations.

Beside the problems introduced by conversion and chain-length dependent rate coefficients, there are additional challenges with systems where two types of radicals with distinctly different reactivities occur, as is known since long from ethylene polymerization. It is now generally accepted[13] that this difficulty also intervenes in acrylate polymerization where secondary propagating radicals (SPRs) are transformed into tertiary midchain radicals (MCRs) which propagate and terminate less rapidly than SPRs. This conclusion is based on experimental[28,41–54] and theoretical[55–58] evidence. The situation is further complicated by the back transformation of MCRs into SPRs through monomer addition which results in a dynamic interconversion between secondary and tertiary radicals by backbiting and MCR propagation steps. To comprehensively describe acrylate polymerization, MCR formation and the subsequent reaction pathways of tertiary radicals have to be implemented into the kinetic scheme. Besides initiation, propagation and termination of SPRs, backbiting, propagation from MCR position, and two additional termination steps need to be considered. For the associated rate coefficients only rough estimates were available before 2007.[47,51]

Water-soluble homopolymers and copolymers are of high technical importance because of their wide-spread application in hydrogels, thickeners, viscosifiers, flocculants, membranes, coatings, etc.[59] Mostly, these polymers are obtained from FRP in aqueous solution. Water-soluble monomers of particular technical relevance are acrylic acid (AA), methacrylic acid (MAA), and *N*-vinyl pyrrolidone (NVP). Investigations into the free-radical rate coefficients for polymerizations of these monomers in aqueous as well as organic solutions are scarce.[16] Significant changes of the rate coefficients are expected as a consequence of the action of hydrogen bonds between monomer, polymer, growing radicals, and water. The complexity may be further enhanced in case that ionic interactions come into play. This requires the additional consideration of the degree of ionization for monomer, polymer, and free-radical species.

First studies into the kinetics of FRP in aqueous phase date back to the work of Katchalsky and Blauer in the early 1950s.[60] In the 1970s and 1980s, polymerizations in aqueous solution were investigated mostly by Russian scientists, as reviewed by Gromov et al.[61,62] Only a few individual rate coefficients have been determined by combining stationary methods with the instationary rotating sector technique. The quality of the so-obtained data may however be rather insufficient and reported data exhibit an enormous scatter.[63–65] During recent years, the PLP-SEC technique has been used extensively for k_p measurements in aqueous phase and reliable k_p values[8] became available for AA,[66–69], MAA,[66] *N*-*iso*-propyl acrylamide (NIPAm)[70] and acrylamide (AAm).[71] The implementation of aqueous-phase SEC into PLP-SEC studies on water-soluble monomers[67] brought a significant improvement of k_p determination, as molecular weight distributions of polymer samples from PLP could be measured directly without the need for carrying out polymer modification reactions to produce samples which may be subjected to SEC analysis in organic phase.[66] Such polymer modification may give rise to changes of the MWD and thus may result in unreliable k_p values.[67]

The thesis in hand is mainly devoted to the propagation and termination kinetics in aqueous solution polymerization of MAA (Chapters 6 and 8),[15,72–75] NVP (Chapters 7 and 9), and AA[52] studied via PLP-SEC and SP-PLP-NIR, respectively. MAA and NVP are perfectly suited for systematic kinetic studies, as the produced polymers are well soluble in water and in both cases no backbiting reactions occur which would necessitate the use of an extended kinetic scheme. However, MCR formation has to be considered in AA polymerization as is indicted by the problems[55–57] faced in PLP-SEC experiments at elevated temperatures[52,66–69]. Moreover MCR build up was directly demonstrated by ESR spectroscopy.[41] As already mentioned, the kinetic description of acrylate polymerization is not even satisfactory adressed for polymerization in organic phase. Thus, new experimental methods were developed which are based on both, PLP-SEC experiments under extended variation of laser pulse repetition rate (Chapter 11)[52,53] and ESR spectroscopic measurements under stationary, pseudo-stationary[54] and instationary polymerization conditions (Chapter 12). These techniques were first applied to polymerizations of acrylic acid esters, mainly butyl acrylate (BA), in organic phase to prevent superposition with added complexity met in aqueous-phase polymerization. The understanding of the general kinetic trends observed in aqueous-solution polymerization of MAA and NVP is combined with the results for BA polymerization and with theoretical arguments (Chapter 10) toward describing the k_p and k_t data measured for AA (Chapter 13).