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Pulsed-laser studies on the free-radical polymerization kinetics of styrene in microemulsion

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Introduction

The accurate and precise knowledge of propagation rate coefficients k_p is of paramount importance for a detailed understanding of the kinetics and mechanisms of, for example, emulsion polymerizations (see e.g. refs. ^{1–3}). Several methods of obtaining k_p have been reviewed and one of the more reliable methods is pulsed-laser polymerization (PLP)^{4–8}. This method comprises the generation of radicals through a photoinitiator, activated by a laser pulse. When termination of radicals in-between laser pulses is not complete, the pulse interval determines the growth time of a definite part of the chains. Because their termination predominantly occurs just after the radical concentration has been sharply increased through a successive laser pulse, this termination is mainly one by very short chain radicals. Superimposed onto a distribution of polymer terminated in-between laser pulses, the molecular weight distribution (MWD) resulting from PLP may therefore contain additional peaks resulting from chains that have grown an integer multiple of the time between pulses.

The location of these peaks may in principle be measured by means of gel-permeation chromatography (GPC) and may be used to determine the propagation rate coefficient k_p for free-radical polymerizations in bulk. According to Olaj et al.^{4–6}, the molecular weight M_{ip} at the low-molecular-weight side inflection point of the additional peaks is a good measure of k_p and, again according to Olaj et al.^{4–6}, is largely unaffected by the termination coefficient or the mode of termination. It may be formulated as

$$M_{ip,i} = i \cdot M_m \cdot k_p \cdot c_m \cdot t_0 \quad (1)$$

where M_m is the molecular weight of a monomeric unit, c_m the monomer concentration, t_0 the time between successive laser pulses and $i = 1, 2, 3, \dots$. A comprehensive description of the kinetics of pulsed-laser initiated polymerization in bulk, including the variation of the MWD of the resultant polymer, was also given by Aleksandrov et al.⁹. It allows for a straightforward simulation of molecular weights $M_{ip,i}$ and their variation with parameters such as repetition rate of pulses, concentration of radicals and monomer and kinetic coefficients for chain propagation and termination. This

simulation once again provides evidence that the $M_{ip,i}$ are good measures of k_p , provided "bulk-typical" parameters are used within the calculations¹⁰⁾.

In heterogeneous polymerization systems, like emulsion polymerization, the fate of the radicals is influenced by the fact that the radicals are compartmentalized. Especially interesting are the optically transparent microemulsions where, besides chemical initiation and initiation through γ -radiation, photochemical initiation can also be applied. One of the first examples of the use of γ -radiation to initiate a microemulsion was published in¹¹⁾ 1981. Mann¹²⁾ extended the study of this system in which styrene in combination with cetyltrimethylammonium bromide is used in a microemulsion. He concluded that, in this system, chain termination occurs primarily by chain transfer to styrene and by bimolecular combination of growing polymer chains¹²⁾.

Relatively few reports on photopolymerization in emulsions (e.g.^{13,14)}) and microemulsions (e.g.^{15,16)}) in which initiation was continuous have appeared so far. Holdcroft and Guillet introduced pulsed-laser polymerization in microemulsions in 1990¹⁷⁾, where non-stationary state kinetics was studied using an oil-soluble photoinitiator. It was found that, evidently due to compartmentalization of radicals and in contrast to PLP in homogeneous polymerization systems, "mutual combination of small polymer radicals" in-between two laser pulses and the resulting low-molecular-weight tailing of the MWD's was suppressed. One might therefore speculate that the chance of finding multimodal MWD's should increase with PLP in microemulsions.

A preliminary consideration of possible concentrations of radicals within the droplets of a microemulsion appears to be useful at this point: If an oil-soluble photoinitiator is used, one must expect a minimal initial concentration of one radical per successfully initialized monomer droplet. While two radicals are usually formed on each initiator decomposition, it is normally assumed, that an effective initiation, i. e. polymerization itself, can only be attained when initiator fragments escape rapid termination by even more rapid diffusion out of the original solvent cage. This might be equivalent to an exit of at least one of the primary radicals out of a monomer droplet because of the small droplet sizes in the case of microemulsions. Such a mechanism is normally assumed to explain low efficiencies of initiation by oil-soluble initiators in oil-in-water emulsions^{13,18,19)} or microemulsions²⁰⁾. This appears to be logical with respect to quadratic averaged distances of about²¹⁾ 1 μm typically covered by an initiator fragment or, in general, a small molecule in a typical low-molecular-weight liquid on the time scale of one propagational step, typically in the order of 1 ms. The covered distance of 1 μm surpasses the dimensions of microemulsion droplets by orders of magnitude, not taking into account the surfactant barrier, so that it does seem to be logical in principle to assume an "escape termination by exit" for at least some radicals, even if very high termination frequencies have to be taken into account within the droplets. For instance, with a radical concentration of $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ and a typical termination coefficient of $10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ a termination frequency of 10 kHz would result. Radical concentrations at such a high or even higher level are said to be quite normal with microemulsions, at least theoretically. If microemulsions with droplet diameters of 10 nm, 25 nm or 50 nm were prepared, the resulting "one radical per droplet" concentrations would roughly be $3 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $2 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ or

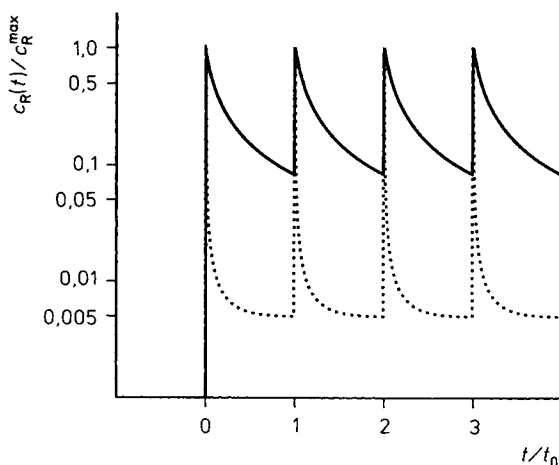
$3 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. Assuming

- a laser energy of the order of 10^{-8} mol of photons per pulse (see below),
- a reaction volume of 1 cm^3 and
- a transformation effectivity of about 5% which would roughly correspond to
 - 1) a typical transmission of 90% of the laser light with respect to the absorbance of the photoinitiator,
 - 2) a production of two primary radicals per photon and
 - 3) an effectivity of transformation of primary radicals into growing chain radicals of 25%,

initiating radical concentrations for PLP experiments in bulk are estimated to be typically in the order of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$. Thus, radical concentrations may be several orders of magnitude higher with respect to the volumes of monomer compartments of monomer-in-water microemulsions as compared to corresponding mean concentrations of radicals in bulk monomer if diameters of monomer droplets are sufficiently small.

When compared to the radical concentration profile as produced by PLP in a homogeneous polymerization system, the corresponding profile in a microemulsion is therefore estimated to consist of two separate decay curves (Fig. 1): For PLP in microemulsions the radical concentration should start at a very much higher level (c_R^{max} in Fig. 1) and, according to a second-order rate law, decays much more rapidly compared with the homogeneous system at short times. At longer times, on the other hand, when the number of droplets containing only one single radical that has escaped termination — e. g. as a result of radical exit — increases, the decay may become slower; this is because bimolecular termination of radicals in the homogeneous phase is estimated to proceed more rapidly than interparticle termination, which either involves exit of radicals and entry into other growing particles or coagulation of growing particles¹²⁾.

Fig. 1. Schematic representation of the estimated radical concentration profile as produced by pulsed laser polymerization in microemulsion (.....) as compared to the expected profile in a homogeneous polymerization system (—) as a function of time t . The time interval of the laser pulses is t_0 , c_R^{max} corresponds to the pseudo steady-state maximum concentration of radicals just after the laser pulse (which is normally attained after a few pulses⁹⁾) and $c_R(t)$ is the radical concentration at time t



Experimental part

Styrene (Merck) was distilled under reduced pressure. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Aldrich), sodium chloride (Riedel-de Haën) and Aerosol OT (AOT = sodium bis-ethylhexylsulfosuccinate^{a)}, Sigma) were used without further purification.

The microemulsions were prepared at 60 °C as an oil-in-water mixture of styrene with the initiator DMPA, stabilized with AOT. The polarity of the water phase was adjusted with a 10 wt.-% solution of NaCl. As a result of detailed experimental screenings with these compounds, a part of a phase diagram was constructed (Fig. 2).

A pulsed excimer laser (Radiant dyes, RD-EXC-150) was operated at 308 nm (XeCl). The pulse energy reaching the fluid was 4 mJ, which corresponds to approximately 10^{-8} mol of photons per flash. The pulse width was 15–25 ns.

Microemulsions with calculated dimensions of 6 to 30 nm were prepared. The diameter d was calculated according to

$$d = \frac{6 \cdot m_{\text{mon}} \cdot M_{\text{surf}}}{m_{\text{surf}} \cdot A_{\text{surf}} \cdot N_{\text{A}} \cdot \rho_{\text{mon}}} \quad (2)$$

where M_{surf} = molecular weight of surfactant, A_{surf} = specific area of surfactant molecule taken as²²⁾ 85 \AA^2 , N_{A} = Avogadro's number, ρ_{mon} = density of monomer²³⁾ = $0,8702 \text{ g} \cdot \text{mL}^{-1}$ and m_{mon} and m_{surf} are the used amounts of monomer and surfactant.

The reactions were carried out in quartz tubes which, after being purged with He, were sealed with a quartz window. The tube was thermostated at $60 \text{ }^\circ\text{C} \pm 0,2 \text{ }^\circ\text{C}$. Pulse repetition rates were between 0,1 and 10 Hz and accumulated polymerization times were 1 or 5 min.

Directly after laser irradiation, the microemulsions were mixed with 10 mL of dichloromethane (Lichrosolv, Merck) with a small amount of 2,2,6,6-tetramethyl-1-piperidinyloxy^{b)} free radical (TEMPO, Janssen Chimica) as inhibitor. To break the emulsion, aluminium oxide (Aluminium oxide 90, Merck) and sodium carbonate (Riedel-de Haën) were added.

The organic phase was filtered over a $0,45 \text{ }\mu\text{m}$ filter and analyzed by means of gel-permeation chromatography. Five Waters Ultrastragel columns (500 \AA , 10^3 \AA , 10^4 \AA , 10^5 \AA , 10^6 \AA) were used at $25 \text{ }^\circ\text{C}$. The eluent was dichloromethane (Lichrosolv, Merck) with a flow rate of

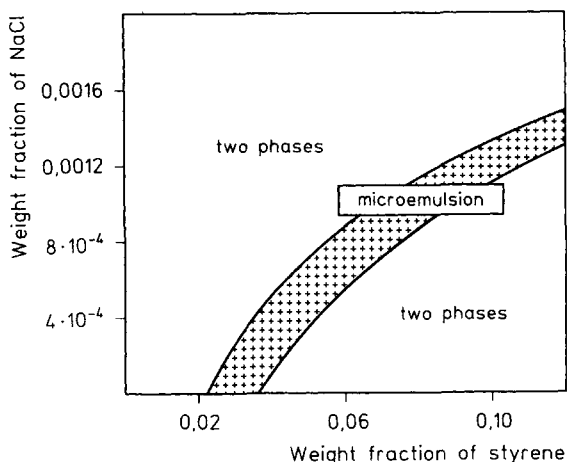


Fig. 2. Schematic representation of the partial phase diagram for the water-styrene-AOT microemulsion system with a constant amount of water (20 g) and AOT (1 g) at 60 °C. The weight fractions of NaCl and of styrene are expressed in grams per gram of microemulsion

a) IUPAC name: sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate.

b) IUPAC name: 2,2,6,6-tetramethylpiperidin-1-oxyl.

$0,8 \text{ mL} \cdot \text{min}^{-1}$. Calibrations were performed with polystyrene standards (Polymer Standards Service). A Waters R 401 differential refractometer and a Waters 440 absorbance detector (wavelength 254 nm) were used.

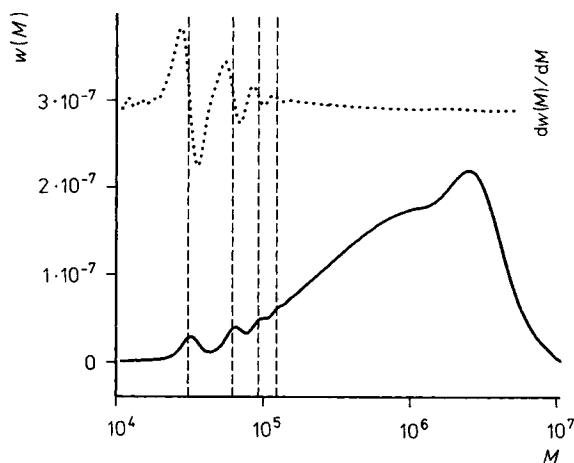
Conversions were determined from the calibrated refractometer signals.

Results and discussion

A typical gel-permeation chromatography curve for PLP in microemulsion is shown in Fig. 3. When compared to a GPC curve of a PLP experiment in bulk (Fig. 4) there are two striking differences: The low-molecular-weight tailing is not present in the microemulsion experiments, whereas a dominant high-molecular-weight peak appears, which extends up to molecular weights $> 10^7$. Note that the ordinate scales differ by one order of magnitude in Figs. 3 and 4. There is evidently little tendency of termination in-between laser pulses in the microemulsion experiment. If individually compartmentalized radicals are not prone to termination, the main mechanism of chain termination in the absence of reinitialization will be transfer to monomer. In accordance with modern model conceptions²⁴⁾, bimolecular termination may then occur via transfer of radical activity to monomer followed by exit of a low-molecular-weight radical and reentry into another growing particle. The high-molecular-weight peak in Fig. 3, together with the relatively small amount of polymer originating from radical chains that survived only a few subsequent laser pulses, are understood as an indication of a low probability of reinitialization of growing particles in subsequent laser pulses, thus giving rise to transfer-dominated growth of a corresponding large fraction of the radicals. PLP of microemulsions therefore appears to represent a promising new approach towards determining of transfer rate coefficients for free-radical polymerizations¹⁰⁾, a proposal which contradicts the suggestion of Holdcroft et al.¹⁷⁾, who excluded the possibility of chain transfer accounting for chain termination.

While only two "additional peaks" are observed for the homogeneous PLP in Fig. 4, four are recognized for the microemulsion experiment in Fig. 3, a result which is demonstrated even more convincingly in the inserted derivatives $dw(M)/dM$. This is

Fig. 3. Experimental molecular weight distribution (MWD) for a pulsed-laser polymerization of a water-styrene-AOT microemulsion with $t_0 = 0,1 \text{ s}$ at 60°C (see Experiment ME (2) in Tab. 1). The inserted derivative $dw(M)/dM$ is computed by numerical differentiation and plotted in arbitrary units (dotted line). $w(M)$ is polymer weight fraction of molecular weight M . Broken vertical lines correspond to $i \cdot M_m \cdot k_p \cdot c_m \cdot t_0 = i \cdot 30808 \text{ g} \cdot \text{mol}^{-1}$ with $i = 1, 2, 3$ and 4 ; (cf. Eq. (1))



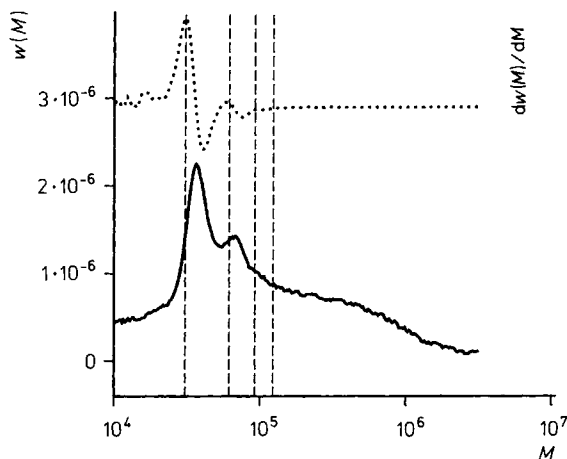


Fig. 4. Experimental molecular weight distribution (MWD) for a pulsed-laser polymerization of bulk styrene with $t_0 = 0,1$ s at 60°C (see Experiment BU (3) in Tab. 1). The inserted derivative $dw(M)/dM$ is computed by numerical differentiation and plotted in arbitrary units (dotted line). $w(M)$ is the polymer weight fraction of molecular weight M . Broken vertical lines correspond to $i \cdot M_m \cdot k_p \cdot c_m \cdot t_0 = i \cdot 30808 \text{ g} \cdot \text{mol}^{-1}$ with $i = 1, 2, 3$ and 4 ; (cf. Eq. (1))

worth mentioning with respect to experimental precision, because the chain length independence of propagation rate coefficients for free-radical polymerizations is meanwhile generally accepted, i. e., the larger the number of additional peaks resulting from PLP, the more precise the determination of k_p is estimated to be.

Results of the present investigation are summarized in Tab. 1. The monomer concentration at zero conversion in the microemulsion droplets was taken as the bulk value ($8,356 \text{ mol} \cdot \text{L}^{-1}$ at²³⁾ 60°C). This appears to be logical in that the physical properties of neat liquids in dispersed phases of microemulsions are supposed to be identical to the bulk properties of the liquids if droplet diameters are above²⁵⁾ 2 nm . Conversions were kept below or around 5% . The corresponding decreases in monomer concentration as a consequence of conversion were nevertheless corrected as described by Schnöll-Bitai et al.²⁶⁾

From Tab. 1, a mean value of $k_p = 354 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ results for the bulk experiments, which agrees very well with a benchmark value of $k_p = 356 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at⁷⁾ 60°C . Within an experimental uncertainty of roughly $\pm 5\%$, no dependency of k_p on the pulse repetition rate, i. e. the radical chain length, is observed. A mean value of $k_p = 339 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ has been derived from PLP experiments in microemulsions, without taking into account the experiments on emulsions with a droplet diameter of $5,7 \text{ nm}$. A very clear decrease in k_p with the droplet diameter can be observed in the two experiments with the smallest droplets ($5,7 \text{ nm}$). Although less obvious, the same trend appears to be present in the experiments with larger droplet diameters in Tab. 1. For illustrative purposes, the bulk values for $i \cdot M_m \cdot k_p \cdot c_m \cdot t_0$ are indicated for $i = 1, 2, 3$ and 4 in Figs. 3 and 4 as broken lines using the mean value of $k_p = 354 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. With respect to these values, the inflection points of the MWD in Fig. 4 are systematically shifted towards lower molecular weights. Since k_p is usually assumed to be the same in the monomer phase of emulsion polymerization systems as in the extended bulk monomer phase, the first conceivable explanation of this result might be that the monomer concentration c_m within the droplets is lower than the

Tab. 1. Pulsed-laser polymerizations of styrene at 60°C in microemulsions (ME) prepared with 20 g of water and 1 g of AOT and in bulk (BU) with 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator

Experiment ^{a)}	m_{sty} g	d nm	[DMPA] ^{d)} mol · L ⁻¹	$N_i^{e)}$	$N_m^{f)}$	f ^{g)} Hz	t ^{h)} min	ϕ ⁱ⁾ in %	k_p ^{j)} L · mol ⁻¹ · s ⁻¹
ME (1)	2,20	13,2	$1,4 \cdot 10^{-2}$	10	5924	5	1	1,2	328
ME (2)	2,20	13,2	$1,4 \cdot 10^{-2}$	10	5924	10	1	2,6	338
ME (3)	0,95	5,7	$1,7 \cdot 10^{-1}$	8	488	5	5	1,0	260
ME (4)	0,95	5,7	$1,7 \cdot 10^{-1}$	8	488	5	5	1,0	265
ME (5)	3,01	18,2	$5,3 \cdot 10^{-3}$	10	15886	5	5	6,5	340
ME (6)	4,73	30,8	$4,7 \cdot 10^{-2}$	433	76995	5	5	3,7	351
BU (1)	—	—	$1,2 \cdot 10^{-3}$	—	—	5	5	0,1	360
BU (2)	—	—	$5,3 \cdot 10^{-3}$	—	—	5	5	0,1	351
BU (3)	—	—	$1,4 \cdot 10^{-2}$	—	—	10	1	0,1	352

a) Kind and (number) of experiment.

b) Mass of styrene added to 20 g of water and 1 g of AOT to form the microemulsion.

c) Diameter of microemulsion droplets.

d) Concentration of DMPA.

e) N_i = number of initiator molecules per microemulsion droplet.

f) N_m = number of monomer molecules per microemulsion droplet.

g) f = frequency of laser pulse repetition.

h) t = cumulative polymerization time.

i) Fractional monomer conversion.

j) Propagation rate coefficient k_p as determined from the inflection points of the molecular weight distributions after correction for conversion²⁶⁾.

monomer concentration in bulk. Holdcroft et al.¹⁷⁾ indeed reported a somewhat lower c_m than was theoretically calculable from their microemulsion recipe. According to these authors, this result is of limited significance, because benzene was used as a solvent and 1-pentanol as a co-surfactant, hindering the straightforward calculation of the theoretical c_m . Moreover, the method of determination of c_m appears to be questionable: The products $k_p \cdot c_m$, which, according to Eq. (1) should be determined from the inflection points of MWD's so far, were determined from peak maxima without comment. Additionally, no reference is given with respect to k_p resulting from the PLP of bulk styrene, so that an eventual GPC miscalibration may directly enter into c_m .

As neither solvent nor co-surfactant were used in the preparation of our microemulsions, which had sufficiently large droplet diameters as to ensure bulk phase physical properties²⁵⁾, we did not have to take into account dilution of the monomer in the droplets. Therefore we looked for effects of very large local radical concentrations on the determination of k_p by means of simulations according to Aleksandrov et al.⁹⁾. It turned out¹⁰⁾ that, while assuming typical low-conversion rate coefficients of termination, Eq. (1) is suited for the determination of k_p from the inflection points within moderate initial concentrations of radicals up to $10^{-7} \text{ mol} \cdot \text{L}^{-1}$ per laser pulse, as is the case in the standard PLP-evaluation method as applied to bulk polymerization. The k_p -relevant molecular weight approaches the peak value of the PLP-resultant additional peaks, the more so, the higher the initial concentrations of radicals per laser pulse, as is the case with PLP-initiated radicals in microemulsion droplets.

Another factor necessary for a detailed understanding of PLP kinetics in microemulsions is the variation of initiator and monomer concentration in the locus of polymerization with the amount of locally formed polymer. Note, for instance, that with respect to theoretical local conversions within isolated droplets, the degree of polymerization $k_p \cdot c_m \cdot t_0$, which is approximately equal to 440 for the experiments with the smallest droplet diameters, may not be reached until (nearly) complete conversion of the droplets. Irrespective of this, the maxima of the first, second, third, and even higher additional peaks appear at molecular weights that correspond to concentrations of neat styrene at 60°C ¹⁰⁾, provided $k_p = 354 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

Conclusions

The pulsed-laser polymerization of microemulsions differs from that in homogeneous systems because of the compartmentalization of the radicals. More peaks resulting from bimolecular termination of laser-generated radicals are observed, giving more precise information for the propagation rate coefficients. For an accurate determination of k_p from polymer resulting from PLP in microemulsions, simulations which account for the especially high initial concentration of radicals after the laser pulse¹⁰⁾ in microemulsions are, however, suggested. Furthermore, PLP with microemulsions apparently permits specific kinetic aspects of the microemulsion polymerization like transfer to monomer and influence of droplet size on bimolecular termination¹⁰⁾, to be studied in detail.

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