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## Monte Carlo simulation of the chain length distribution in pulsed-laser polymerization experiments in microemulsion

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### SUMMARY:

The Monte Carlo method has been used for numerically simulating pulsed-laser polymerization (PLP) in microemulsion, in order to establish if a shift from inflection point to peak maximum as the best measure of the propagation rate constant,  $k_p$ , will occur theoretically. Termination is assumed to be instantaneous in the simulations as droplet sizes can be very small in microemulsions. From the results of the simulations it is found that instantaneous termination indeed causes the peak maximum to become the best measure of  $k_p$ . From these results it can be deduced that in bulk it is not simply the Poisson-broadening that causes the peak maximum to yield an overestimation of  $k_p$ . This overestimation is rather caused by the fact that the termination rate is finite leading to an asymmetrical peak in the molecular weight distribution. In combination with broadening this yields the inflection point to be the best measure of  $k_p$  in the bulk.

### Introduction

Recently a lot of effort has been put into the determination of the rate constants of propagation  $k_p$  for all kinds of (co-)monomer systems with a pulsed laser (see e.g. refs. <sup>1–7</sup>). Aleksandrov and coworkers <sup>8</sup>) were the first to determine mathematically the molecular weight distribution (MWD) resulting from irradiation of a monomer sample with a pulsed laser and to actually perform the experiment. However, Olaj et al. <sup>9</sup>) were the first to correlate the MWD directly with  $k_p$ . During these pulsed-laser polymerization (PLP) experiments, laser pulses (with a pulse length of ca. 20 ns) generate radicals out of a photoinitiator. The polymeric radicals formed directly after a pulse undergo termination during the dark period between two laser pulses. When this termination is not complete, the growing chains left are mainly terminated by very short radicals generated during the next pulse. As this termination is predominant, it results in a peak in the MWD, determined by the time between pulses, superimposed on the distribution resulting from termination during the dark period. As some polymeric radicals may survive two or more pulses, additional peaks could be present at integer multiples of the characteristic chain length.

The resulting MWD can be measured with gel-permeation chromatography (GPC) and the location of the additional peaks can be determined. Peaks are expected at chain lengths  $L_{0,i}$  given by <sup>9</sup>)

$$L_{0,i} = i \cdot k_p \cdot [M] \cdot t_0 \quad (1)$$

where  $L_0$  is the chain length of the polymer formed corresponding to the time between two laser pulses,  $[M]$  the monomer concentration,  $t_0$  the time between two consecutive

laser pulses, and  $i = 1, 2, 3, \dots$ . Closer inspection by Olaj et al.<sup>9)</sup>, using analytically derived equations to describe the resulting MWD, led them to suggest that, because of the statistical character of polymerization reactions leading to a Poisson-broadening of the peaks, it is not the peak maximum but the inflection point at the low-molecular-weight side of the peaks that provides a good measure of  $k_p$ . Note that it is not the Poisson distribution itself that causes the shift of the best measure of  $k_p$  to the inflection point, but the combination of this broadening with the asymmetry of the peak in the theoretical MWD curve; without Poisson-broadening the rise of the peak is infinitely steep while its descent has a finite slope. Olaj et al.<sup>9)</sup> showed that this inflection point as a measure of  $k_p$  is largely unaffected by the termination coefficient or the mode of termination, within the error of GPC.

In order to look deeper into the location of the measure of  $k_p$ , Deady et al.<sup>10)</sup> use numerical integration to solve a system of differential rate equations describing the PLP experiment, which naturally leads to Poisson-broadening<sup>11)</sup>. They conclude that the simulations confirm the robustness and reliability of the PLP method using the inflection point. The radical-time profiles in these simulations reach the pseudo-stationary state<sup>9)</sup> after two pulses. However, because of the use of a limited set of differential equations, a reaction is needed in which all growing polymeric radicals above some arbitrary chain length are combined as a composite species. Hutchinson et al.<sup>11)</sup> use a more efficient algorithm and are able to incorporate more equations allowing simulation until higher degrees of polymerization. Such a restriction in chain length for growing polymeric radicals is absent in a Monte Carlo simulation. Here the only constraint is on the total number of events taking place, like propagation reaction or transfer reaction to monomer. With a sufficiently large number of repetitions of such events the statistical uncertainty of these simulations can be eliminated.

Lu et al.<sup>12)</sup> give a general algorithm for an exact stochastic Monte Carlo simulation of radical polymerizations in bulk or solution, including PLP. They conclude that a pseudostationary state is reached after two pulses. O'Driscoll et al.<sup>13)</sup> also performed Monte Carlo simulations in bulk or solution, trying to explain experimental findings in PLP. The pseudostationary state was reached after 2 to 3 pulses in the simulations. They found that the MWD indeed consists of two distributions: the distribution of polymer formed during the dark period and the additional PLP peaks. They also concluded that taking the inflection point as a measure of  $k_p$  is accurate to within 2 to 3%.

In this work the Monte Carlo simulation is applied to PLP in microemulsion. The first report on PLP in an emulsion system is given by Holdcroft et al.<sup>14)</sup>. They used PLP to determine the styrene concentration in microemulsion droplets,  $C_m$ . However, these authors used the peak maximum instead of the inflection point as a measure of  $k_p$ , without any comments. They also did not describe any bulk experiments to determine  $k_p$ , so that any GPC errors will enter into  $C_m$  directly.

Manders et al.<sup>15)</sup> determined the  $k_p$  for styrene from experiments in bulk and as a function of droplet size in microemulsion. Bulk phase properties in microemulsions were ensured<sup>16)</sup> as all droplet diameters were above 2 nm. As no cosurfactant or cosolvent was used,  $C_m$  was taken as the bulk value. A slight decrease in the apparent  $k_p$  could be found with decreasing droplet size, which becomes very evident for the

small microemulsion droplets with a 5,7 nm diameter. A possible explanation<sup>15)</sup> could be the small volume the radicals are confined to in the microemulsion droplets in relation to the rate of termination. The experiments strongly indicate that the best measure of  $k_p$  shifts from inflection point to peak maximum. With these experiments in mind the simulations were designed. The experiments were performed with an oil-soluble initiator<sup>15)</sup> so all radicals are formed in the microemulsion droplets. This is also assumed in the simulations. One complication of this system is the pairwise formation of radicals necessitating an extra radical process rendering one radical inactive in that particular droplet, e. g. exit or transfer to surfactant. Furthermore it is not clear whether the two radicals formed from 2,2-dimethoxy-2-phenylacetophenone, the initiator actually used in the experiments<sup>15)</sup>, are equally capable of initiating a polymer chain. In the simulations these processes are implicitly taken into account by the generation of single radicals. If the radical loss processes are not infinitely fast these processes will also contribute to the broadening of the GPC trace but will not influence the general conclusions drawn from the simulations.

Manders et al.<sup>15)</sup> suggest that chain transfer to monomer is the most important termination event for the compartmentalized radicals in the microemulsion droplets during PLP experiments. For zero-one emulsion systems, in which chain transfer is the sole mechanism of chain termination, the number-based molecular weight distribution  $n(M)$  scales with<sup>17)</sup>

$$n(M) \sim \exp \left[ - \frac{k_{tr}}{k_p} \frac{M}{M_m} \right] \quad (2)$$

where  $k_{tr}$  is the rate constant of transfer to monomer,  $M$  the molecular weight of the polymer and  $M_m$  the molecular weight of the monomer. A plot of the natural logarithm of  $n(M)$  against the molecular weight  $M$  then has a slope equal to  $-k_{tr}/(k_p \cdot M_m)$ .

It is the objective of this paper to establish if a shift from inflection point to peak maximum as the best measure of  $k_p$  indeed occurs also theoretically in the PLP of microemulsions. The simulation model can be checked using the possibility to determine  $k_{tr}/k_p$ . In the next sections, the simulation algorithm as well as the results of the simulations will be described.

### The simulation procedure

In this work an approach to Monte Carlo simulations was employed according to Mann<sup>18)</sup>. This method was previously described by Bunker et al.<sup>19)</sup> as a hybrid method. However, Mann<sup>18)</sup> was able to prove the validity of this method as an exact stochastic simulation, making Monte Carlo simulations simpler than the method developed by Gillespie<sup>20)</sup>, which was used in the simulations of polymerization by Lu et al.<sup>12)</sup>

In this approach an interval  $\tau$  is used as the time step in the calculations.  $\tau$  is the time between kinetic events. For a system in which polymeric radicals only undergo propagation or chain transfer, the next reaction will occur after a time interval, which is given by<sup>18)</sup>

$$\tau = \frac{1}{[M](t) \cdot (k_p + k_{tr})} \quad (3)$$

where  $[M]$  is calculated as a function of time, enabling  $\tau$  to be calculated throughout the polymerization.

A flowsheet of the simulation for PLP in a microemulsion is shown in Fig. 1. As there is no dependence on droplet/particle diameter, the algorithm is also applicable to particles in a zero-one emulsion system. A system is simulated in which ND is the number of droplets present. A laser pulse generates N radicals which are distributed randomly over the droplets. Immediate termination occurs when a radical is already present in a droplet, otherwise the droplet is initialized. This immediate termination is assumed because of the very small volumes the two radicals are confined to in a microemulsion droplet. To reduce computing time in the simulations, bimolecular termination was assumed to be a disproportionation reaction.

From the input parameters L0, KP and KTR, representing  $L_0$ ,  $k_p$  and  $k_{tr}$ , it is possible to calculate the number of reaction steps between two successive laser pulses NR, assuming constant  $[M]$ , with Eqs. (1) and (3) according to

$$NR = \frac{t_0}{\tau} = L_0 \cdot \frac{k_p + k_{tr}}{k_p} \quad (4)$$

With  $k_p$  and  $k_{tr}$  also the probability of transfer to monomer, PTR, is calculated according to the relation<sup>18)</sup>

$$PTR = \frac{k_{tr}}{k_p + k_{tr}} \quad (5)$$

After NP pulses the number-based molecular weight distribution  $n(M)$  is given as output. The resulting dead polymer chains are stored for each chain length individually.

Simulations were written in C using a pseudo-random number generator with a linear congruential algorithm and at least 32-bit integer arithmetic. Simulations were performed on an Alliant FX/2816 or a Silicon Graphics Challenge computer. Computation times were extremely long for the simulation in which the model was validated by determining the ratio of  $k_{tr}$  over  $k_p$  from the simulated MWD. At large chain lengths, only a limited number of growing polymeric radicals are present. Because of this and the statistical character of Monte Carlo simulations, a large number of pulses is necessary for noise reduction at these large chain lengths. For these simulations 25 000 pulses were simulated. With 1 000 pulses a sufficient resolution for the determination of the location of the inflection point was already reached.

During the simulations, ND was set at 5 000, L0 ranged from 1 000 and 10 000, KP from 100 to 1 000, KTR from 0,05 to 0,1. For a particular set of the previous parameters, N was set at 1, 1 000 or 5 000.

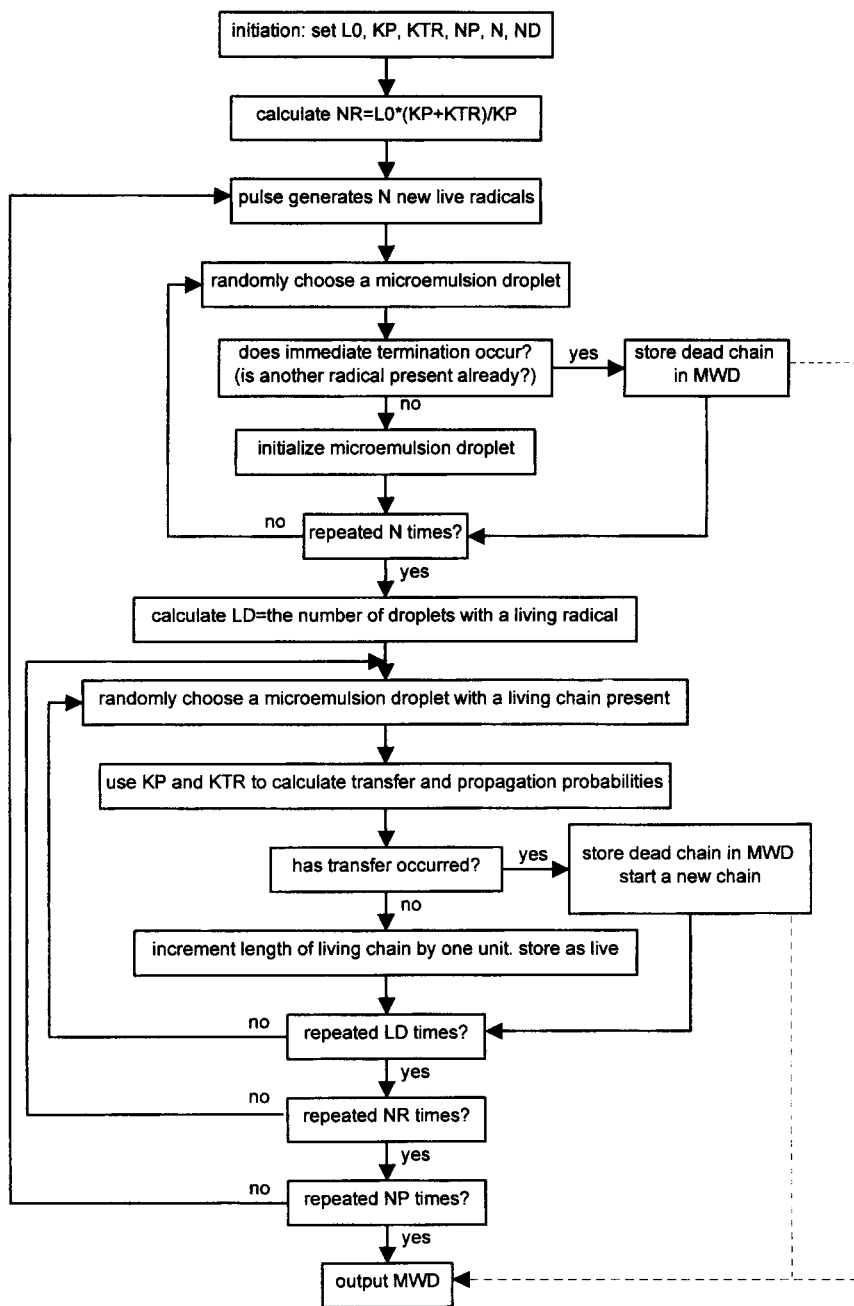


Fig. 1. Flow sheet for the Monte Carlo simulation of the pulsed-laser polymerization in micro-emulsion

## Results and discussion

In Fig. 2 the influence of the number of radicals that are generated in a laser pulse on the MWD is given. When the number of radicals generated in a laser pulse equals the number of microemulsion droplets present, a number of PLP peaks can be observed. However, when only a very small number of radicals, compared to the number of droplets, is generated, no PLP peaks can be observed and the number-based MWD is continuously decreasing. Here, bimolecular termination is successfully suppressed, leaving transfer as the sole chain stoppage reaction. Experimentally, this

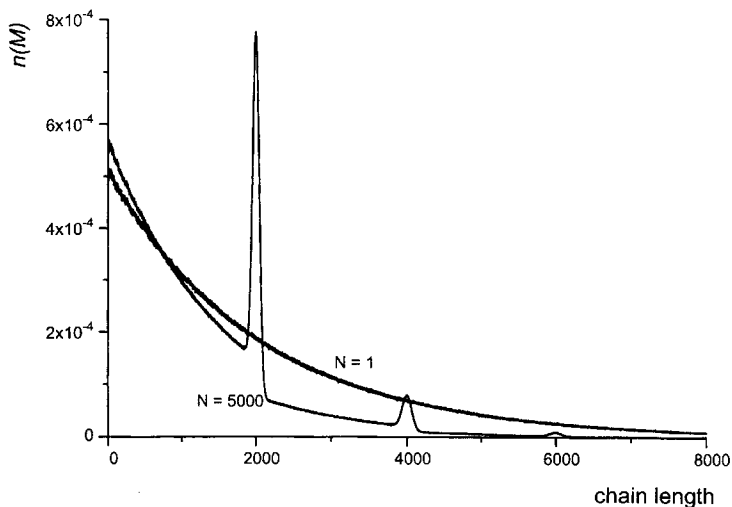


Fig. 2. Theoretical number-based molecular weight distributions for PLP in microemulsions with  $L_0 = 2000$ ,  $K_P = 100$ ,  $K_{tr} = 0,05$ ,  $N_P = 25\,000$ ,  $N_D = 5000$ ;  $N = 1$  or  $N = 5000$

has been done<sup>21)</sup> using an initiator concentration yielding one initiator molecule per microemulsion droplet. In Fig. 3 the logarithm of  $n(M)$  of this transfer-dominated simulation is plotted as a test of the simulation algorithm. The slope, derived from the line in Fig. 3, yields a ratio of  $k_{tr}/k_p$  of  $5,00 \cdot 10^{-4}$ . This is in excellent agreement with the ratio of  $k_{tr}/k_p$  of  $5 \cdot 10^{-4}$  calculated from the input parameters.

Closer inspection of the PLP peaks in Fig. 2 reveals that the peak maximum is a better measure of  $k_p$  than the inflection point at the low-molecular-weight side of the PLP peaks. In Tab. 1 a comparison is made between the  $k_p$  derived from the inflection point and from the peak maximum for different sets of input parameters. The peak maximum is indeed always very close to the ideally expected chain length.

The reason for the fact that in this simulation the peak maximum is the better measure of  $k_p$  is the assumption that termination is immediate. This immediate termination leads to a symmetrical peak in the MWD, which can be represented by a delta-function with Poisson-broadening, leaving the position of the peak maximum on

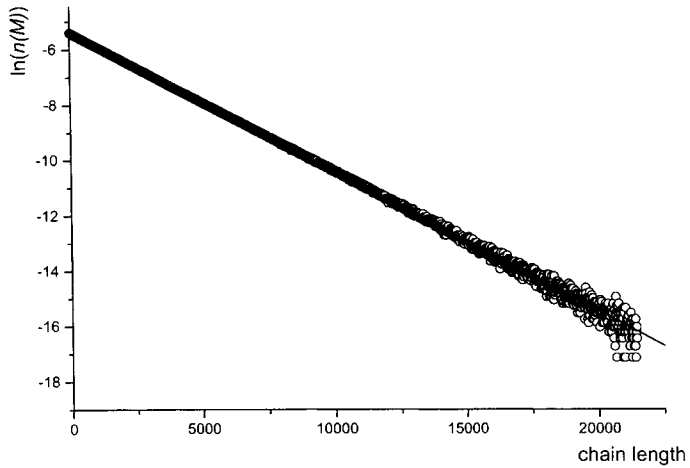


Fig. 3. Natural logarithm of the theoretical number-based molecular weight distribution for PLP in microemulsions with  $L_0 = 2\,000$ ,  $KP = 100$ ,  $KTR = 0,05$ ,  $NP = 25\,000$ ,  $ND = 5\,000$  and  $N = 1$ . The ratio of  $k_{tr}/k_p$  derived from the slope is  $5,00 \cdot 10^{-4}$ . The line represents the linear fit from which this ratio has been derived

Tab. 1. Comparison of  $k_p$  derived from inflection point and peak maximum from number-based molecular weight distributions (MWD) simulated with Monte Carlo methods for the pulsed-laser polymerization in microemulsion for 5 000 microemulsion droplets ( $ND = 5\,000$ ), assuming instantaneous termination

No. <sup>a)</sup>	$L_0$ <sup>b)</sup>	$k_p$ <sup>c)</sup> mol · L <sup>-1</sup>	$k_{tr}$ <sup>d)</sup> mol · L <sup>-1</sup>	N <sup>e)</sup>	NP <sup>f)</sup>	$k_p$ (i. p.) <sup>g)</sup> mol · L <sup>-1</sup>	$k_p$ (max.) <sup>h)</sup> mol · L <sup>-1</sup>
1	2 000	100	0,05	1	25 000	— <sup>i)</sup>	— <sup>i)</sup>
2	2 000	100	0,05	1 000	10 000	97,7	99,7
3	2 000	100	0,05	5 000	25 000	98,0	99,8
4	2 000	100	0,1	5 000	1 000	98,0	99,8
5	2 000	200	0,1	5 000	1 000	195,7	199,6
6	1 000	100	0,1	5 000	1 000	94,4	99,9
7	10 000	100	0,1	5 000	1 000	— <sup>i)</sup>	— <sup>i)</sup>
8	10 000	1 000	0,1	5 000	1 000	996,3	999,9

- a) Number of the simulation.
- b)  $L_0$  = chain length calculated according to Eq. (1).
- c) Propagation rate constant  $k_p$  used in simulations.
- d) Transfer to monomer rate constant  $k_{tr}$  used in simulations.
- e) N = number of radicals generated in a laser pulse.
- f) NP = number of pulses simulated for a particular simulation.
- g)  $k_p$  (i. p.) =  $k_p$  derived from the inflection point at the low-molecular-weight side of the first PLP peak in the simulated MWD and calculated according to Eq. (1) with  $[M] \cdot t_0$  calculated from the input parameters  $L_0$  and  $k_p$ .
- h)  $k_p$  (max.) =  $k_p$  derived from the peak maximum of the first PLP peak in the simulated MWD and calculated according to Eq. (1) with  $[M] \cdot t_0$  calculated from the input parameters  $L_0$  and  $k_p$ .
- i) Almost no growing polymeric radicals left.



$L_0$ . This assumption is valid for the very small volumes that can be reached with microemulsion polymerization. In other simulations, describing bulk phase polymerization or polymerization in solution, termination is not instantaneous.

From simulations according to O'Driscoll et al.<sup>13)</sup> in bulk some dependence of the place of the inflection point can be seen. The ratio  $KT0$ , which is given by

$$KT0 = \frac{k_t}{k_p \cdot [M] \cdot N_{Av} \cdot V} \quad (6)$$

with  $N_{Av}$  the Avogadro constant and  $V$  the simulated volume, varies in the simulations and might imply a change in  $k_t/k_p$ . While increasing the value for  $k_t/k_p$  and therefore also  $KT0$ , the inflection point shifts to lower chain lengths, but for real monomer systems with real values for rate constants this shift will be very small in bulk or solution, so there the inflection point still is the best measure of  $k_p$ .

## Conclusions

In microemulsions the droplet diameters can be very small, leading to the assumption that immediate termination occurs whenever a second radical is formed in the same droplet. This prevents any propagation steps to occur between the generation of a second radical in a microemulsion droplet and termination. With this assumption in Monte Carlo simulations, the maximum of the molecular weight distribution is the best measure of  $k_p$  in PLP experiments in microemulsion. In bulk, however, part of the polymeric radicals will undergo some propagation steps between the generation of new radicals and the termination of the growing chains. This leaves an asymmetrical peak in the MWD, which in combination with Poisson-broadening is making the peak maximum an overestimation. The rate of termination is thus capable of influencing the position of the inflection point. However, using accepted values for  $k_t/k_p$  in simulating PLP in bulk, the inflection point still is the best measure of  $k_p$ .

- 1) M. Buback, L. H. Garcia-Rubio, R. G. Gilbert, D. H. Napper, J. Guillot, A. E. Hamielec, D. Hill, K. F. O'Driscoll, O. F. Olaj, J. Shen, D. Solomon, G. Moad, M. Stickler, M. Tirell, M. A. Winnik, *J. Polym. Sci., Part C: Polym. Lett.* **26**, 293 (1988)
- 2) M. Buback, R. G. Gilbert, G. T. Russell, D. J. T. Hill, G. Moad, K. F. O'Driscoll, J. Shen, M. A. Winnik, *J. Polym. Sci., Part A: Polym. Chem.* **30**, 851 (1992)
- 3) R. G. Gilbert, *Pure Appl. Chem.* **64**, 1563 (1992)
- 4) T. P. Davis, K. F. O'Driscoll, M. C. Piton, M. A. Winnik, *Macromolecules* **23**, 2113 (1990)
- 5) S. Deibert, F. Bandermann, J. Schweer, J. Sarnecki, *Makromol. Chem., Rapid Commun.* **13**, 351 (1992)
- 6) P. Pascal, M. A. Winnik, D. H. Napper, R. G. Gilbert, *Makromol. Chem., Rapid Commun.* **14**, 213 (1993)
- 7) B. R. Morrison, M. C. Piton, M. A. Winnik, R. G. Gilbert, D. H. Napper, *Macromolecules* **26**, 4368 (1993)
- 8) A. P. Aleksandrov, V. N. Genkin, M. S. Kitai, I. M. Smirnova, V. V. Sokolov, *Kvantovaya Elektron. (Moscow)* **4**, 976 (1977); Engl. Transl.: *Sov. J. Quantum Electron.* **7**, 547 (1977)
- 9) O. F. Olaj, I. Bitai, F. Hinkelmann, *Makromol. Chem.* **188**, 1689 (1987)

- <sup>10)</sup> M. Deady, A. W. H. Mau, G. Moad, T. H. Spurling, *Makromol. Chem.* **194**, 1691 (1993)
- <sup>11)</sup> R. A. Hutchinson, J. R. Richards, M. T. Aronson, *Macromolecules* **27**, 4530 (1994)
- <sup>12)</sup> J. Lu, H. Zhang, Y. Yang, *Makromol. Chem., Theory Simul.* **2**, 747 (1993)
- <sup>13)</sup> K. F. O'Driscoll, M. E. Kuindersma, *Macromol. Theory Simul.* **3**, 469 (1994)
- <sup>14)</sup> S. Holdcroft, J. E. Guillet, *J. Polym. Sci., Part. A: Polym. Chem.* **28**, 1823 (1990)
- <sup>15)</sup> B. G. Manders, A. M. van Herk, A. L. German, J. Sarnecki, R. Schomäcker, J. Schweer, *Makromol. Chem., Rapid Commun.* **14**, 693 (1993)
- <sup>16)</sup> R. Schomäcker, *Nachr. Chem. Tech. Lab.* **40**, 1344 (1992)
- <sup>17)</sup> G. Lichti, R. G. Gilbert, D. H. Napper, "Theoretical predictions of the particle size and molecular weight distribution in emulsion polymerizations", in "Emulsion Polymerization", I. Piirma, Ed., Academic Press, New York 1982
- <sup>18)</sup> R. Mann, *Ph. D. Thesis*, Sydney (1992)
- <sup>19)</sup> D. L. Bunker, B. Garrett, T. Kleindienst, G. S. Long, *Combust. Flame* **23**, 373 (1974)
- <sup>20)</sup> D. T. Gillespie, *J. Phys. Chem.* **81**, 2340 (1979)
- <sup>21)</sup> J. Schweer, A. M. van Herk, R. J. Pijpers, B. G. Manders, A. L. German, *Macromol. Symp.*, in press; *3rd International Symposium on Radical Copolymers in Dispersed Media*, April 17–22, 1994, Lyon, France