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PULSED LASER POLYMERIZATION OF STYRENE
IN COMPARTMENTALIZED SYSTEMS

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Abstract: Pulsed laser polymerizations of styrene were performed in microemulsion droplets and in latex particles. From the molecular weight distribution of the resultant polymer either the propagation rate coefficient in the droplets or the monomer concentration in the particles could be determined. Furthermore for microemulsion droplets with a low initiator concentration the rate coefficient for transfer to monomer could be determined. Because in very small particles the termination rate can be very high, instantaneous termination may occur, leading to a shift of the low molecular weight inflection point as the best measure of the propagation rate coefficient to the maximum in the molecular weight distribution.
Performing pulsed laser polymerization experiments directly in emulsion systems gives specific information on the special features associated with doing polymerizations in heterogeneous and compartmentalized systems.

INTRODUCTION

The propagation rate coefficient (k_p) is a very important kinetic parameter that is of paramount importance for understanding kinetics and mechanism of for example emulsion polymerizations. Several methods of obtaining k_p have been reviewed and one of the more reliable methods is the pulsed laser polymerization (PLP) (Refs. 1,2). This method comprises the generation of radicals through a photoinitiator, activated by a laser pulse. The time between pulses determines the growth time of a major part of the chains because termination occurs preferably just after the radical concentration has been increased through a laser pulse. The molecular weight distribution contains peaks of chains that have grown an integer multiple of the time between pulses.

Other radical reactions that can occur (in addition to propagation) inbetween two pulses in the same experiment and contribute to the molecular weight distribution are *inter alia* (bimolecular) termination. In heterogeneous polymerization systems like microemulsions and latices the fate of the radicals is also influenced by the fact that the radicals are compartmentalized.

Holdcroft and Guillet for the first time introduced the pulsed laser polymerization in microemulsions in 1990 (Ref. 3). Different from homogeneous polymerization systems, for PLP in microemulsions, conditions can be met where, as a result of compartmentalization of the radicals, bimolecular termination inbetween two laser pulses is suppressed resulting in the absence of the low molecular weight tailing that normally appears in PLP experiments in bulk and solution (Refs. 3,4). Termination of growing chains by chain transfer to monomer may then be the main chain stopping mechanism and the molecular weight distribution will contain unique information on the transfer rate coefficient to monomer.

The chain length for long chains terminated by small laser induced radicals is given to a very good approximation by the simple equation (Ref. 5)

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

where: $L_{0,i}$ is the chain length of the polymer formed by linear growth in the time between two laser pulses, k_p is the propagation rate coefficient, $[M]$ the monomer concentration at the site of polymerization, t_0 is the time between two successive laser pulses and $i = 1,2,3,....$ Olaj (Ref. 5) suggested that the inflection point at the low molecular weight side of the peaks gives a good measure of k_p.

However, in experiments with very small microemulsion droplets indications were found

that the best measure of k_p shifts from the inflection point to the peak maximum (Ref. 4). This was also confirmed by theoretical calculations using a deterministic approach of Alekandrov et.al. (Ref. 6,7) as well as a Monte-Carlo approach (Ref. 8). On the other hand, when k_p is known, PLP may also be used to obtain monomer concentrations in microemulsion droplets and in latex particles (eq. 1) (Ref 9).

In microemulsion droplets and latex particles the radical concentration decay profiles following the rapid increase in radical concentration after a laser pulse is supposed to consist of two decay curves (Ref. 4). The first one refers to bimolecular termination within (micro)emulsion droplets or particles. The second decay curve involves exit of a radical and entry into another particle followed by bimolecular termination. When the number of radicals per particle becomes less than two, this "termination after exit" process can be the only one and thus the concentration decay may be much lower than in a homogeneous system. The important mechanism of chain stoppage (not influencing the radical concentration) in this time interval will be chain transfer to monomer. Termination of growing chains by newly laser generated radicals within the particle under consideration must however not necessarily happen at the occurance of the subsequent pulse, but can also happen at some arbitrary later pulse (expressed by i in eq. 1).

For a zero-one emulsion system, in which transfer to monomer is the dominant mechanism of termination, the number molecular weight distribution n(M) scales to (Ref. 10)

$$n(M) \propto \exp\left(-\frac{k_{tr}}{k_p} \cdot \frac{M}{M_m}\right) \tag{2}$$

where k_{tr} is the rate coefficient 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 at the limit of high molecular weight then has a slope of $-k_{tr}/(k_p \cdot M_m)$. This method of obtaining k_{tr} is also useful in pulsed laser experiments as shown by Monte-Carlo simulations for microemulsions (Ref. 7) and experiments on transfer from methyl methacrylate to triethylamine (Ref. 11).

Pulsed laser experiments, to our knowledge, have never been performed so far in latex particles. In this article it is described how one can obtain:

(1)   the chain transfer rate coefficient, and

(2)   the monomer concentration in microemulsion droplets and latex particles knowing the propagation rate coefficient k_p, or inversely,

(3)   when the monomer concentration in the particles is known, k_p in the locus of

polymerization.

EXPERIMENTAL PART

Styrene (Merck) was distilled under reduced pressure. 2,2-dimethoxy-2-phenylace-tophenone (DMPA, Aldrich), sodium chloride (Riedel-de Haën), sodium persulfate (Merck), sodium carbonate (Riedel-de Haën), Aerosol OT (AOT = sodium bis-ethyl-hexylsulfosuccinate, Sigma) and Aerosol MA-80 (AMA-80 = sodium dioctylsulfosuccinate, Cyanamid) 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 Aerosol OT, the polarity of the water phase was adjusted with a 10% solution of NaCl. A partial phase diagram has been published before (Ref. 4).

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 ca. 10^{-8} mol of photons per flash. The pulse width was 15-25 ns.

Microemulsions with calculated dimensions of 6 to 30 nm diameter were prepared as previously described (Ref. 4). The latices were prepared in a steel reactor with a volume of 1 litre at a temperature of 80 °C and a stirring speed of 500 r.p.m.

Tab. 1 shows the recipes for the two latices prepared, together with the radii r_o of the unswollen particles which were determined by ultracentrifugation (Ref. 13).

Tab.1 Recipes for the latex preparations and particle radius

Nr	water	styrene	Na_2CO_3	$Na_2S_2O_8$	AMA-80	r_o
	g	g	g	g	g	nm
1	691	243,6	0,33	11,42	0,72	55,15
2	694	243,4	0,03	1,04	0,07	245,5

Dow uniform latices (SERVA) with a radius of 35 nm, 99 nm, and 227 nm were used as received. The reactions were carried out in quartz tubes which, after being purged with He, were sealed with a quartz window. In the experiments where the latex particles were swollen with excess styrene (containing about 0,1 M DMPA) the laserbeam was led through a second quartz tube inside the quartz tube with the latex. In this way it was prevented that the laser energy was absorbed by the monomer layer. The sample was

thermostated at 22 or 60 ± 0,2 °C. Pulse repetition rates were between 0.1 and 10 Hz and accumulated polymerization times were between 1 and 60 minutes. Conversions were always below 5%.

To break the microemulsions, aluminium oxide (Aluminium 90, Merck) and sodium carbonate were added. To break the latices 6 ml 5% sulfuric acid was added. The samples were then mixed with 10 mL dichloromethane (Merck) with a small amount of 2,2,6,6-tetramethylpiperidinooxy (TEMPO, Janssen Chimica) as inhibitor.

The organic phases were filtered over a 0,45 µm filter and analyzed by means of gel-permeation chromatography. Waters Ultrastyragel columns were used at 22 or 25 °C. The eluent was dichloromethane (Lichrosolv, Merck) with a flow rate of 0,8 mL 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. Densities of styrene and polystyrene at different temperatures were taken from the literature (Ref. 12)

RESULTS AND DISCUSSION

Microemulsion experiments to obtain k_{tr}

It was previously shown that in contrast to PLP experiments in bulk, the low-molecular weight tailing is not present in MWD of microemulsion made polymer whereas a dominant high-molecular-weight peak appears. This high-molecular-weight peak was attributed to terminated chains formed by transfer to monomer. In the case of a zero-one system the chain transfer rate coefficient can be inferred from this high-molecular-weight part of the MWD in the way described by Lichti et al. (Ref. 10) and Gilbert and coworkers (Ref. 14). If less than one radical per microemulsion droplet is generated by a laser pulse it is expected that transfer to monomer will be the only termination mechanism and therefore the treatment of these data will give the most reliable value for k_{tr}.

An experiment with a calculated microemulsion droplet size of 12 nm and a concentration of DMPA of 4.1 10^{-4} mol per litre of monomer results in an average of less than one molecule of DMPA per microemulsion droplet. By plotting ln (n(M)) versus M in Fig. 1, a slope can be obtained that equals $-k_{tr}/(k_p \cdot M_m)$ (Eq. 2).
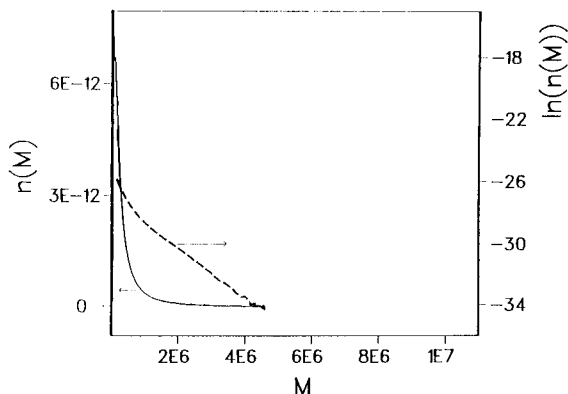
Fig. 1. Molecular weight distribution for a PLP experiment at 60 °C with a droplet diameter of 12 nm, 15 min. pulse laser polymerization time, a pulse laser frequency of 5 Hz, [DMPA] = 4.1 10^{-4} mol l^{-1}. The microemulsion recipe was 20 g water, 1 g AOT and 2 g styrene and NaCl (see Ref. 4).

The resulting slope equals -1.61 10^{-6} which, with k_p of 354 l mol^{-1} s^{-1} (Ref. 4), results in a value of 5.9 10^{-2} l mol^{-1} s^{-1} for k_{tr} of styrene at 60 °C. The slope is obtained by linear regression analysis and is constant over a molecular weight range of 1 10^{-6} to 4 10^{-6}.

A similar analysis of microemulsion experiments described in Ref. 4 with 8 to 10 DMPA molecules per microemulsion droplet yielded values around 3.5 10^{-2} l mol^{-1} s^{-1} at 60°C. These values compare well with the value for k_{tr} of 1.3 10^{-2} l mol^{-1} s^{-1} at 50 °C determined in a similar way in chemically initiated seeded emulsion polymerization (Ref. 14).

Although the latter experiments were performed with higher initiator concentrations, the plots of ln(n(M)) versus M were linear over an even wider molecular weight range of 10^6 to 10^7, thus emphasizing that great care has to be taken when k_{tr} is extracted from such data and further experiments should be undertaken even over a wider range of experimental conditions so that the minimum value for the k_{tr} characteristic slope can be detected (at infinite molecular weight !).

Pulsed laser polymerizations in latex particles to obtain [M]

In microemulsions prepared without cosolvent the monomer concentration equals that of bulk monomer down to droplet diameters of several nanometers (Ref. 4). However, in latex particles the monomer concentration is *inter alia* dependent on particle diameter and determined by the thermodynamic swelling behaviour as described by Morton *et al.* (Ref.

15) for saturation swelling and by Maxwell *et al.* (Ref. 16) for partial swelling.

Provided that the propagation rate coefficient for a given monomer is identical in the homogeneous (or bulk) monomer phase and within the monomer swollen polymer particles of a latex, the following simple relation can be used:

$$[M]_{PLP}^{P} = [M]^{B} \, \frac{L_{o,i}^{P}}{L_{o,i}^{B}} \tag{3}$$

From this equation the monomer concentration $[M]_{PLP}^{P}$ in the latex particles can be obtained by applying PLP to a latex system and by comparing the MWD of the resultant polymer with the MWD of polymer from a PLP experiment in bulk monomer B with known concentration $[M]^{B}$. $L_{o,i}^{P}$ and $L_{o,i}^{B}$ are the chain lengths at the i-th inflection point of the emulsion polymer and bulk polymer MWD, respectively.

Because of the absorption and scattering of the laser light not all particles will actually be irradiated. It is therefore important that the irradiated sample is not mixed too quickly so as to prevent growing particles from entering the dark region of the sample, where they can not be terminated by the radicals generated by the subsequent laser pulse.

As stated before (Ref. 4), to rule out systematic errors caused by any possible GPC miscalibration, k_p was measured again in bulk styrene. At 60 °C k_p was found to be 315 l mol⁻¹ s⁻¹ and at 22 °C k_p was found to be 80 l mol⁻¹ s⁻¹. These values compare well with values calculated from an Arrhenius plot based on the k_p values published by Hutchinson et al. (Ref. 17).

In Fig. 2 the MWD of latex 1 (see Table 2) is shown and the MWD of the second stage polymer can be seen as it evolves as a function of polymerization time.

In Table 2 monomer concentrations, $[M]_{PLP}^{P}$ obtained by using Eq. 3 are given for partial and saturation swelling experiments with latex particles of different diameters. All determinations of $[M]_{PLP}^{P}$ were performed using the molecular weight pertaining to the first low-molecular weight inflection point, although usually one or two extra inflection points could be observed at integer multiples of the molecular weight of the first inflection point.

The resulting monomer concentrations $[M]_{PLP}^{P}$ compare very well with the $[M]_{calc}^{P}$ values calculated from the added amount of monomer for partial swelling.
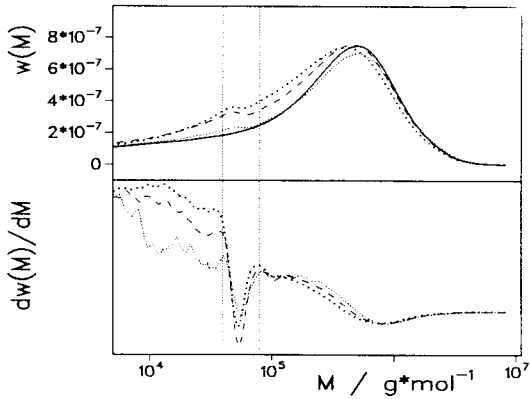
Fig. 2. MWD and derivative of PLP-experiments with seed latex (60°C, 5Hz). Total polymerization time: 0 min (   ), 15 min (------), 30 min (   ), 45 min (-----).
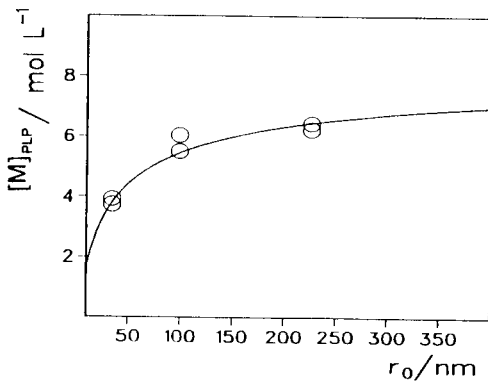

Fig. 3. The dependence of $[M]_{PLP}$ on the particle size (DOW latices). Experimental data (open circles, polymerization time between 10 and 60 min, frequency 5 s^{-1}, [DMPA] = 80 mmol l^{-1}), the line was fitted to the data with the Morton equation (Ref. 12) (κ = 0.324, γ = 72.6 dyne/cm).

Tab.2

Latex	T	υ	Reaction time/min	$[M]^{PC}_{calc}$	$[M]^{P}_{PLP}$
	°C	s^{-1}		mol l^{-1}	mol l^{-1}
1[a]	60	5	30	2.84	2.78
1[a]	60	5	30	2.96	2.50
1[a]	60	5	30	4.07	4.01
1[a]	60	5	30	4.53	4.85
1[a]	60	5	30	4.91	4.91
1[a]	60	5	30	5.29	5.38
1[a]	22	5	90	4.65	4.31
1[a]	60	5	30	4.50	4.29
1[b]	60	5	15	......	6.40
2[b]	60	5	30	......	7.00

a   partial swelling data

b   saturation swelling data, average of several experiments

c   calculated from the amount of styrene present in the sample

The saturation monomer concentrations of Tab. 2 compare well with the data of Tseng et al. (Ref. 18), although differences in surfactant coverage of the latex surface have to be considered. For saturation swelling of three different Dow latices the monomer concentrations were plotted against the particle diameter in Fig. 3. The drawn line is calculated from the Morton equation (Ref. 15), using the styrene/polystyrene interaction parameter $\kappa = 0.324$ and an interfacial tension of $\gamma = 72.6$ dyne cm^{-1}. These results clearly indicate that the PLP-method to determine the monomer concentration in latex particles leads to reliable absolute values and permits to study the effects of e.g. particle size or other parameters like surfactant coverage of the particles on this essential emulsion polymerization parameter. Because monomer concentrations can be determined in reacting systems, information can also be obtained on non-equilibrium monomer concentrations caused by diffusion limitations.

CONCLUSIONS

Depending on the design of the experiment, pulsed laser polymerizations in microemulsions and latex systems provide information on the propagation rate coefficient, the rate coefficient for transfer to monomer, or the monomer concentration, all at the locus of polymerization.

The PLP-method to determine the monomer concentration appears to give an accurate and quick alternative to other methods and it has the advantage of being applicable to undiluted systems even in case that they are not in thermodynamic equilibrium.

Because of the unique feature of compartmentalization of growing radicals in emulsion and microemulsion systems it is possible to largely favour transfer to monomer as the dominant termination mechanism for the laser generated radicals thus facilitating the reliable determination of k_{tr} to monomer.

ACKNOWLEDGEMENT

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