Pulsed Electron Beam Polymerization of Styrene in Latex Particles

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ABSTRACT: The polymerization of styrene in latex particles by means of pulsed high-energy electrons has been studied. Using a sequence of electron beam pulses, periodic initiation is accomplished, similar to that used in pulsed laser polymerization. The larger penetration depth of electron beams offers advantages as compared to laser light in heterogeneous systems since samples do not need to be optically transparent. Therefore pulsed electron beam irradiations are more suitable to study polymerizations homogeneously irradiated in emulsion. From the molar mass distribution of the formed polymer, the monomer concentration in the particles can be determined. Polystyrene particles swollen with styrene were used. A typical dose per pulse was 1.5 Gy. The monomer concentration in 46 nm diameter particles was found to be 6 mol dm^{-3}. Cationic and anionic polymerization of styrene was suppressed by the presence of water.

Introduction

In order to understand the kinetics and mechanism of emulsion polymerizations knowledge of the propagation rate coefficient (k_p) and the monomer concentration is of paramount importance. Several methods of obtaining k_p have been reviewed, and one of the more reliable methods is pulsed laser polymerization (PLP).[1]

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 biradical termination occurs preferably just after the radical concentration has been increased through a subsequent laser pulse.

The molar mass distribution contains peaks of chains that have grown an integer multiple of the time between pulses.

Other radical processes that can occur in the same experiment and contribute to the molar mass distribution are bimolecular termination between two pulses and chain transfer processes.

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 introduced the pulsed laser polymerization for the first time in microemulsions in 1990.[2] Different from homogeneous polymerization systems, for PLP in microemulsions, conditions can be met where bimolecular termination between two laser pulses is suppressed due to compartmentalization of the radicals, resulting in the absence of the low molar mass tailing that normally appears in PLP experiments in bulk and solution.[3] When these conditions in microemulsions are met, besides termination of growing chains by small radicals generated by the laser pulse, termination of growing chains by transfer to monomer is the main chain stopping mechanism and the molar mass distribution contains information on the transfer rate coefficient.[4]

The same approach has also been applied to (nontransparent) latex particles.[4] Although the specific PLP peaks appear in the gel permeation chromatography (GPC) traces, only a very small part of the reactor content can be irradiated and stirring of the contents leads to the total disappearance of the PLP peaks. This is caused by a large "dark" region where termination of the growing chains by newly formed small radicals is less likely. Because mixing is therefore not desirable, temperature gradients in the polymerization cell can occur. This has led to the investigation of high-energy electrons, generated by a pulsed 3 MV Van de Graaff accelerator as a source of initiating radicals that will be investigated in this paper. The 3 MeV electrons have a penetration depth of typically 1 cm water. The penetration depth is independent of optical transparency. To our knowledge the use of a sequence of electron beam pulses to obtain information on k_p and/or monomer concentrations in latex particles has never been reported before. It is known that the presence of water prevents cationic polymerization of styrene and that radicals are responsible for the polymerization.[5,6]

The chain length for the chains terminated by small laser light or electron beam induced radicals is given by the simple equation[7]

$$L_{o,i} = ik_p[M]t_o \tag{1}$$

where $L_{o,i}$ is the chain length (in monomeric units) of the polymer formed in the process of growth in the time between two laser pulses, k_p is the propagation rate coefficient, [M] is the monomer concentration at the site of polymerization, t_o is the time between two successive laser pulses and $i = 1, 2, 3, ...$ for chains that were terminated after the subsequent pulse or survived one, two, etc. subsequent laser pulses before termination, respectively.

Olaj[7] suggested that the inflection point at the low molar mass side of the PLP peaks gives a good measure for $L_{o,i}$ and therefore k_p (provided of course that [M] is known). However, in very small microemulsion droplets, indications were found that the best measure for

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k_p shifts from the inflection point to the peak maximum.[3] The size of the polymer particles in the experiments described in this paper is large enough to be able to use the inflection point.[3]

In regimes where the termination rate is very high, theoretical calculations indeed show that the peak maximum is the best measure for the calculation of k_p.[8,9]

The reason behind using PLP and pulsed electron beam polymerization (PEBP) is to obtain monomer concentrations in heterogeneous systems. When k_p is known, eq 1 can be used to obtain the monomer concentration in microemulsion droplets and in latex particles.[4]

In microemulsion droplets and latex particles the radical concentration profile in the pseudostationary state in the PLP experiments will consist of two regimes of decay curves following the rapid increase in radical concentration during the laser pulse. In the first one just after the rapid increase in the radical concentration, the rate of termination will be high because the radical concentration will be high. The second part comprises the stage where the number of radicals per particle is less than 2, and here the termination rate will be lower that in a homogeneous system because termination involves exit of a radical from one particle and entry into another particle followed by bimolecular termination. In this part the main mechanism of chain stoppage is chain transfer to monomer.

Initiation of polymeric reactions by high-energy electrons is known for decades and has been used extensively in industry for the preparation of plastics and coatings.[10] Also electron beam initiation has been used in emulsion polymerization.[11]

The use of a particular sequence of electron beam pulses results in the formation of polymer which contains material with a molar mass which can be described by eq 1 and therefore opens the possibility in the above mentioned applications of better control of molar mass distribution and connected properties.

Experimental Section

Styrene (Merck) was distilled under reduced pressure. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy), was used as a photoinitiator in the pulsed laser experiments. The seed latex was prepared in a steel reactor containing 450 g of H_2O, 20 g of styrene, 1 g of $NaHCO_3$, 2.9 g of Aerosol-22, and 2.2 g of $K_2S_2O_8$. The reaction was performed at 80 °C and stirred with a turbine stirrer at 250 rpm for 24 h.[4] The resulting latex was dialyzed until the conductivity of the water around the dialysis tubing reached a constant conductivity.

The unswollen particle diameter was determined by TEM photos and has a value of 46 nm with a standard deviation of 9 nm.

For both the PLP and the PEBP experiments the latices were swollen with an excess of styrene for 24 h.

In order to analyze the molar mass distribution (MMD) of the polymer formed during the PEBP and PLP experiments with GPC, 0.1 w/v % solutions in tetrahydrofuran (THF, stabilized, Biosolve, AR) were prepared of each sample which was isolated by freeze drying.

The solutions were filtrated over 0.2 μm filters. The GPC analyses were carried out with two Shodex KF-80M (linear) columns at 40 °C. The eluent was THF at a flow rate of 1 cm^3 min^{-1}. A Waters 410 differential refractometer and a Waters 440 UV detector (254 nm) were used for detection. Narrow-distribution polystyrene standards (Polymers Labs) with molecular weights (M) ranging from 580 to 6.5×10^6 were used for calibration of the columns. After a baseline correction, the GPC chromatograms were converted to a differential log distribution ($w(\log M)$ vs $\log M$) according to the procedure described by Short[12] and fitted with a cubic spline function. From these distributions the maximum in the first derivative was used to obtain values for $L_{0,i}$.

The pulsed laser experiments were performed using a Lambda Physik LPX110iMC pulsed excimer laser at 351 nm (XeF line) with pulse energies of 30 mJ. The width of the pulse was 20 ns. The laser beam (with dimensions of 18 mm × 7 mm) was directly irradiating the sample. The sample was inside a quartz cell with the same dimensions as the laser beam with a path length of 5 mm. The temperature was measured inside the cell with a Pt-100 resistance element (Netsushin, MG-1505), which was protected from direct irradiation by the laser beam.

The pulsed electron beam polymerizations were performed with nanosecond pulses of 3 MeV electrons from a Van de Graaff accelerator described elsewhere.[13]

The cylindrical quartz cell had a diameter of 2 cm and a path length of 5 mm and was thermostated with a metal block surrounding the cell at the bottom and the side.

The width of the pulse was 2 ns (ca. 3 A, 0.27 Gy/nC). Dosimetry was performed using stacked FWT-60 thin film dosimeters.[14]

Values for the propagation rate constant were calculated from the benchmark Arrhenius plot:[15] 82 dm^3 mol^{-1} s^{-1} at 23 °C and 243 dm^3 mol^{-1} s^{-1} at 50 °C.

Results and Discussion

In order to have a high probability of termination after an electron pulse in a compartmentalized system, the pulse should result in the formation or entry of at least one radical per particle on the average.

The radical polymerization in the styrene-swollen polystyrene latex particles may be initiated by radical formation in the latex particles and/or by waterborne radicals (e^-_{aq}, $H^\bullet$, $OH^\bullet$) entering the latex particles. The dose per pulse required to obtain one radical per particle (a minimum value to obtain well-resolved PEBP peaks) can be calculated for both cases.

Using a value for the yield of radicals initiating polymerization in pure styrene of 0.7 (1/100 eV) (0.7×10^{-7} mol/J),[16,17] we can calculate that the average number of radical initiations per particle for particles of 100 nm diameter is equal to 1 for a dose of 48 Gy (384 Gy for 50 nm particles).

Using the yields of formation of e^-_{aq}, $OH^\bullet$ and $H^\bullet$ in water of 2.7, 2.7, and 0.6 (1/100 eV), respectively,[18] we find that at a dose of 2.7 Gy the total number of radicals formed per unit volume is equal to a concentration of particles of 10^{18} particles per liter. Therefore the average number of radicals formed per latex particle per pulse equals 1 at this dose.

In the experiments the dose is varied from ca. 0.3 to 3 Gy. We see that for this range of doses, the fraction of particles where polymerization is initiated directly in the particles is very small (the fraction of particles having no initiation event for a dose of 3 Gy is 0.94 (exp (−3/48)).

We do not know at present precisely which radicals from the aqueous phase contribute to the polymerization and which fraction of the yield formed in the aqueous phase enters the particle leading to successful initiation/termination. If an efficiency of 1 is taken for the water radicals formed to initiate polymerization (which is an overestimate), we find that for ca. 3 Gy the average number of initiations per particle is equal to 1 (37% of the particles has no initiation).

The minimum dose per pulse in the PEBP experiments in order to observe well-resolved PEBP peaks had to be determined experimentally because the number of radicals in a particle has a Poisson distribution and competing reactions can occur.

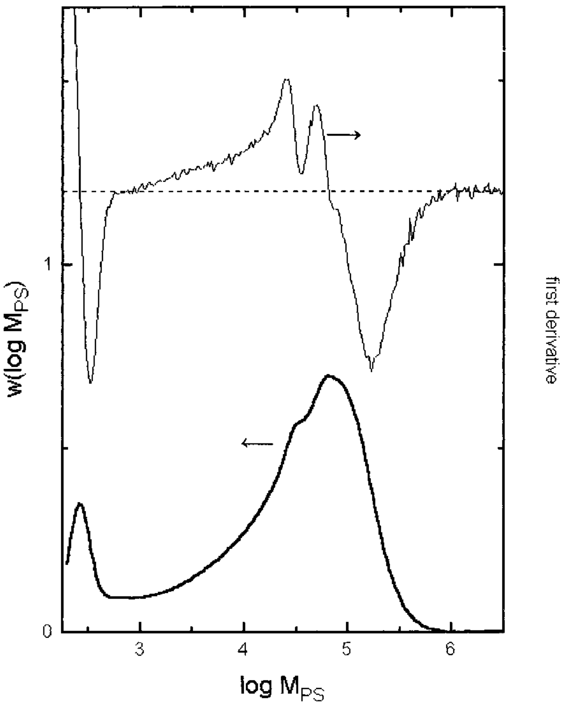

Figure 1. Molar mass distributions obtained from a PEBP experiment of styrene in polystyrene particles of 46 nm diameter, performed at 23 °C, at a frequency of the electron beam pulses of 2 Hz, and with a total amount of pulses of 300. The dose per pulse was 1.51 Gy.

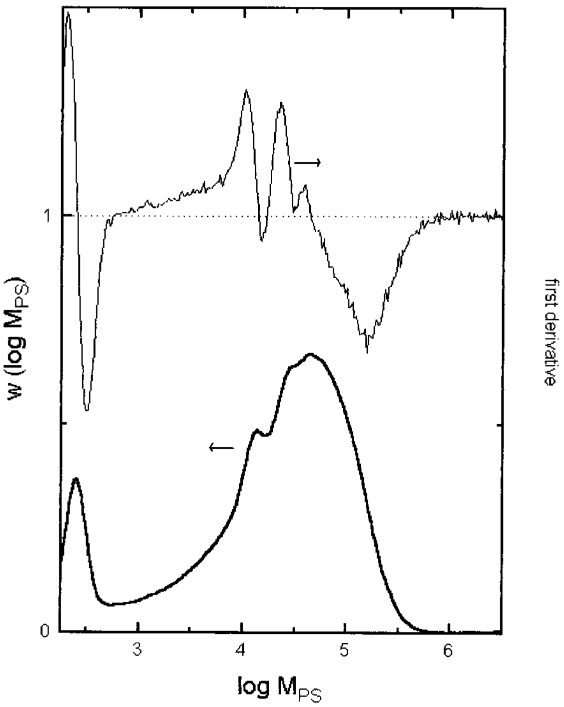

Figure 2. Molar mass distributions obtained from a PEBP experiment of styrene in polystyrene particles of 46 nm diameter, performed at 23 °C, at a frequency of the electron beam pulses of 5 Hz, and with a total amount of pulses of 1000. The dose per pulse was 1.49 Gy.

The optimum dose per pulse turned out to be between 1 and 4 Gy per pulse. Therefore it might be concluded that the main source of initiation is the radicals formed in the aqueous phase. When only the radicals formed in the latex particles would be the main source of initiation, a dose of 384 Gy would be necessary for latex particles of 50 nm to obtain an average of one radical per particle at each pulse. After 300 pulses, on top of the MMD of the seed latex particles, the expected peaks of polymeric materials appeared that can be described with eq 1. Similar experiments were also performed with PLP and the location of the extra peaks was the same for both experiments at the same temperature and frequency.[4]

In Figures 1 and 2 MMD's resulting from experiments at 23 °C are depicted. In Figure 1 a frequency of 2 Hz was used, and in Figure 2 a frequency of 5 Hz was used.

In both MMD's, besides the high molecular weight peaks, a low molecular weight peak is also present at 200−300 Da (2−3 units of styrene). This peak is attributed to cationically initiated chains that were immediately terminated by the water present.

From Figure 2 the inflection point at the low molecular weight side is taken as a measure of $L_{o,1}$ (more clearly visible as a maximum in the first derivative). With $L_{o,1} = 231$, $k_p = 82$ dm^3 mol^{-1} s^{-1}, and $t_o = 0.2$ s, from eq 1 the monomer concentration in the latex particles can be calculated as 5.6 mol dm^3. In Figure 2 a second-order peak can be seen ($i = 2$ in eq 1).

In Table 1 the data for experiments at 23 and 50 °C are given at frequencies of 2 and 5 Hz and with varying numbers of pulses.

The resulting monomer concentrations agree well with literature data.[4]

Conclusions

It is shown that pulsed electron beam polymerization is a method that can be used similarly to pulsed laser polymerizations. Pulsed electron beam polymerization offers an important advantage in that the samples do not need to be optically transparent.

Table 1. Experimental Conditions for the PEBP Experiments and Resulting Monomer Concentration

temp (°C)	dose/pulse (Gy)	frequency (Hz)	no. of pulses	concn (mol dm^{-3})
23	1.53	2	100	5.6
23	1.51	2	300	5.6
23	1.52	2	1000	5.5
23	1.49	5	3000	6.3
50	1.75	2	302	5.9
50	1.73	5	100	6.1
50	1.74	5	300	5.7
50	1.75	5	1000	5.7

Calculations show that the waterborne radicals initiate the emulsion polymerization.

The resulting molecular mass distribution can be related to the product of the propagation rate constant and the monomer concentration in the latex particles similarly to the pulsed laser polymerization experiments that give equivalent results.

In polystyrene latex particles with a diameter of 46 nm the monomer concentration was found to be 5.8 ± 0.3 mol dm^3. In pulsed electron beam polymerizations an additional low molecular weight peak was found that could be attributed to cationically initiated styrene units which rapidly terminated with water.

The PEBP method is similar to the previously introduced method of PLP in the latex system[4,19] to obtain monomer concentrations directly in the reacting latex particles but is more flexible and opens possibilities to large scale production of polymers with a specific molecular mass distribution.

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