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A pulsed light reactor for molecular weight control in free-radical polymerization

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Abstract

A new controlled polymerization reactor is introduced. The reactor design is based on the principles of pulsed initiation polymerization. The 1 l reactor is equipped with a high-voltage UV-stroboscope, the frequency of which can be raised up to 250 Hz. In this reactor pulsed initiation polymerizations of *n*-butyl acrylate were performed. Results indicate that the use of high pulse frequencies in this set-up may resolve problems associated with chain transfer to polymer in the determination of propagation rate coefficients for acrylates at temperatures above 30 °C.

Keywords: Free-radical polymerization; Pulsed initiation; Acrylates; Propagation rate coefficients

1. Introduction

In free-radical polymerization there is a growing need for control of the molecular weight distribution (MWD) of the formed polymer chains. In terms of molecular weight control, much effort is put into the chemical control of polymer growth, for example in the so-called "living" or "controlled" radical polymerization (CRP) techniques, such as nitroxide mediated polymerization [1] and atom transfer radical polymerization [2,3]. Here termination is suppressed by adding a stable counter-radical. This approach still has many drawbacks, among other things that reaction temperatures are rather high and reaction times are rather long. Of course, the most important reason for CRP is the synthesis of block-copolymers. Alternatives are based on rapid chain transfer such as in catalytic chain transfer [4] and radical addition fragmentation transfer [5], but also there problems occur, for example with color of the resulting polymer and introduction of sulfur containing end-groups.

Another method of controlling molecular weight is the use of pulses of radicals rather than a continuous flux of radicals, which is the most widespread method at the moment.

Pulses of radicals can be generated by using a pulsed laser in combination with a photoinitiator, a pulsed electron beam [6] or pulsed ultrasound, which is currently being developed in our laboratories. An additional advantage of pulsed initiation is that it can be readily applied to more complex systems as well, such as supercritical CO_2 [7,8], miniemulsion droplets [9]

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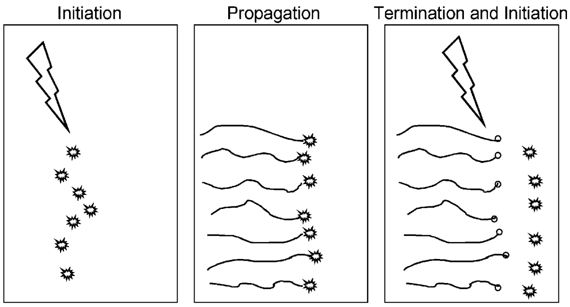

Fig. 1. Principle of pulsed initiation polymerization.

and vesicles [10]. By using pulses of radicals the growth time and thus the molecular weight of the polymer chains can be controlled. The principle is shown in Fig. 1 [11]. At the first pulse radicals are generated, which add monomer so polymer chains start growing. At the arrival of the next pulse most chains will terminate by reaction of long chain polymeric radicals with small photoinitiator derived radicals. The residual small radicals will start the growth of new chains and after many pulses polymer chains with a controlled molecular weight will build up. By adjusting the frequency of the pulsed light source almost any desired molecular weight can be obtained. The degree of polymerization for the chains initiated and terminated by short pulses of radicals, e.g. induced by light in combination with a photoinitiator, is given by the following simple equation [12]

$$L_{0,i} = i \times k_p \times [\mathrm{M}] \times t_p \quad (1)$$

where $L_{0,i}$ is the chain length of the polymer formed in the process of growth in the time between two radical pulses, t_p is the time between two subsequent radical pulses, and $i = 1, 2, 3, \ldots$ The higher order peaks ($i = 2, 3, \ldots$) may occur when growing chains survive the termination by one or more subsequent pulses.

This principle of pulsed initiation/termination (pulsed laser polymerization, PLP) has been used since 1987 as an analytical tool to determine propagation rate coefficients [13–15]. The cells used in these experiments have a volume of a few ml only. Next to pulsed lasers, pulsed UV-lamps have been applied, but only on a few ml scale [16,17]. Now for the first time at the Eindhoven University of Technology a 1 l scale reactor set-up has been constructed in-house on the basis of this principle with the aim to produce larger amounts of polymer. This reactor set-up will allow us to study: (1) the effect of low monomer concentrations on propagation rate coefficients; (2) the aqueous phase polymerization of moderately water soluble monomers; (3) fast propagating monomers as the stroboscope frequency can be raised up to 250 Hz as compared to 100 Hz for a pulsed laser. Moreover, it will provide us with a tool for the controlled synthesis of larger amounts of polymers with a specific molecular weight as the frequency can be varied during the polymerization. This first paper will describe the reactor set-up and some first pulsed initiation polymerization experiments of *n*-butyl acrylate (BA) at high stroboscope frequencies. For comparison, the polymerization of styrene was investigated as well.

2. Experimental

2.1. Materials

2,2-Dimethoxy-1,2-diphenylethane-1-one (DMPA), a commonly-used photoinitiator in PLP, heptane and cyclohexane were all used as received. An inhibitor remover column was used to purify *n*-butyl acrylate (BA). Styrene was distilled under reduced pressure before use.

2.2. Reactor set-up

The reactor set-up is schematically shown in Fig. 2a and b. The reactor consists of a Perkin Elmer FXQ-1307-3 flashlamp, positioned in the center of a double walled stainless steel 1 l reactor. The lamp and high-voltage connections are separated from the reactor contents. A 40 ml quartz tube can be inserted into the reactor in order to perform smaller scale polymerizations. The flashlamp has a maximum frequency of 250 Hz and an intensity of 1430 W. The spectrum of the flashlamp, which is shown in Fig. 3, is centered around 540 nm. Flashlamp frequency (0–250 Hz) and voltage (500–700 V) can be adjusted during the polymerizations via LabView® software. Pulse duration is 600 μs and is independent of stroboscope frequency. Pulse form is presented in Fig. 4. The stroboscope has a quartz jacket through which cooling water is running. The stroboscope is a series triggered flash tube circuit (Fig. 2b). The breakdown voltage of most xenon flash tubes is high, typically 10 kV or more. The practical flash tube circuit utilises a capacitor charger voltage (LS1500, 600 V) which is much lower than the breakdown voltage. Conduction is initiated by application of a high-voltage trigger-transformer circuit. The trigger pulse is typically in the 10–20 kV range with a duration of about 1 μs (150 nS/in. of the length of the tube). The cooling water for the flash tube must be high resistive demineralised water. High resistivity is necessary so the cooling liquid is not conductive; demineralisation prevents deposits from being built up on the outside of the flash tube. Safety and control circuits give the reactor set-up an automatic shut down. The reactor is equipped with a saw-tooth Teflon-coated magnetic disc located at the bottom of the reactor to ensure sufficient mixing. An Ocean Optics optrode is inserted into the reactor for monitoring monomer concentrations.