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Perspectives of aerosol-photopolymerization: Nanoscale polymer particles



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HIGHLIGHTS

- Nanoscale polymer particles were generated by a continuous aerosol-based process.
- By means of photoinitiation, the process could be operated at ambient temperature.
- Photoinitiation resulted in instantaneous start of polymerization reactions.
- By avoiding the usage of surfactants, highly pure polymer particles were produced.
- The process exhibits great potential for multifunctional nanoparticle generation.

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ABSTRACT

Photoinitiated polymerization is employed to produce submicron polymer particles in aerosols. By ultraviolet (UV) irradiation of the aerosol monomer solution droplets, produced with the help of an atomizer, polymerization is initiated by free radical generation. The aerosol process allows the production of surfactant-free polymer particles without any solvent required, while photochemistry results in instantaneous formation of free radicals by cleavage of excited photoinitiator molecules. Furthermore, the initiation can take place independent of temperature, which provides polymerization at ambient temperature. A continuous experimental setup with a flow-through photoreactor is developed, which is characterized by a sub-minute aerosol residence time. The experiments reveal that spherical nanoparticles can be formed as 1-to-1 copy from the monomer droplets.

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1. Introduction

Polymeric (nano)particles have increasingly been raising interest for a number of applications ranging from optics and photonics to nanomedicine. They are used, for example, in combination with inorganic nanofillers for transparent polymers (Althues et al., 2007; Khrenov et al., 2005), or in life sciences as controlled drug release agents (Shi et al., 2010). Different production methods are available to obtain polymer particles. Emulsion polymerization is one of the most often established techniques, where the use of surfactants is required and mostly thermally initiated polymerization is applied. These surfactants may be incorporated in the polymer structure and decrease the product purity (Landfester et al., 1999). After polymerization in wet methods, the particles might have to be separated by downstream processes like

centrifugation or filtration, washed and dried under vacuum (Huang and Brittain, 2001). These process operations consume time and cost.

Polymers as functional materials can also be prepared by photochemical technologies. The use of photons for polymer preparation goes back to the beginning of the 20th century, when Klatt converted vinyl chloride into PVC by light-induced polymerization (Braun, 2001). Photoinitiated dispersion polymerization was successfully applied in aqueous alcohol media to produce submicron polymer particles on a lab-scale (Ye et al., 2002). As an alternative to liquid process routes, polymer particles can also be produced by processes based on aerosols. Aerosol techniques avoid the need of surfactants and downstream processes, permitting integrated processes. Different aerosol-based methods were employed so far. Nebulization-polymerization was performed for producing micrometer-sized polystyrene particles. After nebulization of the liquid monomer to monomer droplets, the droplets were brought into contact with initiator vapor (Shin et al., 1996). Esen and Schweiger (1996) combined the aerosol technique with

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photopolymerization to produce micrometer-sized polymer particles. A multiacrylate monomer mixture containing photoinitiator and binding agents was dissolved in a volatile solvent and dispersed using a vibrating-orifice aerosol generator with the help of nitrogen gas. The generated aerosol droplets were irradiated with black light fluorescent strip lamps (wavelength ≈ 360 nm) to produce highly monodisperse spherical polymer particles with diameters between 5 and 50 μm and smooth surfaces. In a similar work, where the aerosol generator was a modified vibrating-orifice aerosol generator, monodisperse polymer microspheres with diameters between 5 and 100 μm were generated by photopolymerization via UV irradiation as well (Gao et al., 2007). A drawback of the use of a vibrating-orifice aerosol generator is the limited droplet generation rate, leading to low polymer particle concentrations. The photopolymerization kinetics of a multiacrylate monomer droplet being a few micrometers in diameter was investigated on-line with Raman spectroscopy, revealing that a time period of nearly 100 s is required for the complete polymerization (Esen et al., 1996). A number of publications can be found on the photopolymerization kinetics of very fast crosslinking reactions, where polymerization is completed within a few seconds (Andrzejewska, 2001; Anseth et al., 1994; Bowman and Peppas, 1991; Decker, 1992, 2002; Decker et al., 1996; Decker and Moussa, 1990; Kindernay et al., 2002; Kurdikar and Peppas, 1994; Scherzer et al., 2004).

In this work, photoinitiated free radical polymerization of submicron monomer droplets for the generation of spherical polymer nanoparticles is presented. The particles were produced from monomer solution droplets consisting of liquid monomer and dissolved photoinitiator. The size of the polymer particles can be pre-adjusted by the diameter of the monomer droplets since the polymerization process is restricted to the volume of each monomer droplet. No surfactants and any additional solvent were used for the preparation of the monomer droplet aerosol, leading to highly pure polymer particles. The employed aerosol generator produces high concentrations of monomer droplets and has the potential of up-scale. The subsequent photoreactor of this continuous experimental setup can be operated with a sub-minute average aerosol residence time. Such a short reaction time necessitated fast overall polymerization kinetics. This can be accomplished by different combinations of initiation and propagation rates. The initiation rate in photochemical systems can be adjusted by photoinitiator concentration, photon exitance, and photophysical properties of the photoinitiator. Photochemistry also permits a continuous aerosol process. Fast propagating monomers could be polymerized with and without a crosslinker, but monomers exhibiting a low propagation rate coefficient required the addition of a crosslinker or a comonomer to accelerate the overall polymerization rate. A quasi-monochromatic UV excimer irradiation source (Kogelschatz, 1990) allowed instantaneous generation of free radicals and avoided the need of higher reaction temperatures, which would be required for thermally initiated systems. Lower reaction temperatures favor thermodynamically the polymerization process and lead to less droplet evaporation rates as well. Aerosol-photopolymerization also offers the potential of producing multicomponent materials.

2. Experimental

2.1. Chemicals and materials

Methyl methacrylate (MMA, Sigma-Aldrich, 99% purity) and butyl acrylate (BA, Sigma-Aldrich, 99% purity) were employed as monomers. Irgacure 907 (Methyl-1[4-(methylthio)phenyl]-2-morpholinopropan-1-one, Sigma-Aldrich, 98% purity) and

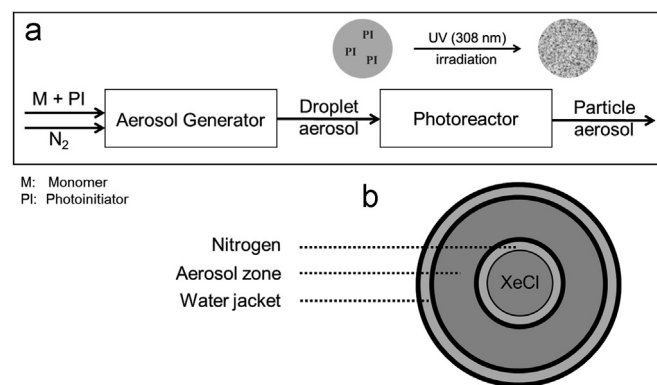


Fig. 1. (a) Scheme of the continuous experimental setup for aerosol-photopolymerization, and (b) schematic cross-section view of the photoreactor.

1,6-hexanediol diacrylate (HDDA, Alfa Aesar, 99% purity) were chosen as the photoinitiator and crosslinker, respectively. All chemicals were used as received except for copolymerization experiments. Pre-packed columns (Sigma-Aldrich) were used for inhibitor removal.

2.2. Process

The continuous experimental setup consists of two main components, an aerosol generator and a flow-through photoreactor, as depicted in Fig. 1(a). The monomer solution was prepared by dissolving the photoinitiator (PI) in the liquid monomer (M) without using any additional solvent. The monomer solution was sprayed with nitrogen gas in an atomizer to generate the droplet aerosol. This droplet aerosol was passed through the photoreactor, where free radicals are generated upon UV irradiation for the polymerization process. The cylindrical flow-through photoreactor with negative irradiation geometry is in-house constructed and consists of concentric HSQ 300 quartz glass tubes. The cross-section of this photoreactor is schematically presented in Fig. 1(b). The custom-made XeCl excimer irradiation source (Radium Lampenwerk, Wipperfürth, Germany) is placed in the center and surrounded by the inner quartz glass tube. The annular gap in between is flushed with nitrogen as cooling gas. Photopolymerization reactions take place in the annular gap between the inner and outer quartz tubes. A water jacket serves as the temperature control in the outer zone. The outer envelope is made of Plexiglas.

The aerosol generator consists of a two-component nozzle. Depending on the nozzle inlet pressure of nitrogen, which can be varied between 1 and 6 bars, the average aerosol residence time in the photoreactor can be varied between 15 and 60 s. In contrast, the time scale of aerosol generation lies within milliseconds. Therefore, the process residence time can be regarded as that in the photoreactor.

The employed XeCl excimer irradiation source emits quasi-monochromatic at 308 nm (width of half height ≈ 3 nm) with a radiant exitance of 10 mW/cm² at the envelope surface. The effective irradiation length of the photoreactor is 32 cm. Polymer particles leaving the photoreactor were collected either dry on a PTFE filter membrane with 50 nm average pore diameter or wet by transfer into water.

2.3. Particle characterization

For scanning electron microscopy images, Hitachi S-4500 and LEO 1530 were employed. The values of acceleration voltage can be found on the corresponding SEM images. A drop of the particle suspension was dropped onto a membrane (Whatman, Nucleopore

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