



# Hybrid miniemulsion photopolymerization in a continuous tubular reactor—A way to expand the characteristics of polyurethane/acrylics

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## ABSTRACT

Waterborne polyurethane (PU)/acrylic hybrids were synthesized by photoinitiated miniemulsion polymerization carried out in a continuous tubular reactor. Almost complete conversion was achieved in short residence time (<5 min) using low concentrations of photoinitiator (<0.48 wt%) and modest incident light irradiance (<7 mW/cm<sup>2</sup>). The hybrid was formed by simultaneous free radical polymerization and addition polymerization, through the reaction of the isocyanate groups of the PU with the hydroxyl groups of the acrylic monomers. It was found that this process is more flexible than the classical semicontinuous miniemulsion polymerization allowing the synthesis of a wide range of polymer characteristics (gel fraction and sol molecular weights) using the same PU/acrylics formulation.

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## 1. Introduction

Hybrid polymer–polymer latexes are of great interest because of their superior properties as compared to those of the individual polymers [1–4]. Miniemulsion polymerization is the method of choice to synthesize polymer–polymer hybrid latexes, particularly when they are produced by different polymerization techniques, e.g., free radical and step-growth polymerizations [5–8]. Over the past 30 years, this attractive technology has been extensively investigated and several reviews have been published [9–12]. Semicontinuous miniemulsion polymerization has been used to synthesize polyurethane (PU)/acrylic waterborne hybrids for pressure sensitive adhesives of remarkable shear resistance at high temperature [13,14]. These hybrids were produced by polymerizing a mixture of (meth)acrylic monomers in the presence of either a vinyl terminated polyurethanes [4,7,14,15] or/and isocyanate terminated PUs [13,16]. In the latter case, the monomer mixture contained a monomer with functional groups able to react with the isocyanate. The free radical polymerization was initiated with thermal and redox initiators. This limits the range of temperatures at which the polymerization of the (meth)acrylates can be carried out, because even though polymerization of (meth)acrylates can be started at low temperature [17,18], the process often lacks reproducibility. Photoinitiation overcomes this limitation as it provides a very fast production of radicals at a wide range of temperatures.

In addition, it provides spatial and temporal control of the polymerization, as radicals are only produced where and when the UV/vis lamp is turned on. Photoinitiated polymerization in dispersed media (mostly aqueous) is an active area of investigation with examples in microemulsion [19–32], miniemulsion [33–38] and emulsion [39–44]. These photopolymerizations were carried out in batch and semibatch reactors. However, the limited penetration depth of the light makes stirred tank reactors not suitable for this type of polymerization. This effect is more pronounced in opaque systems, such as emulsion or miniemulsion, in which light scattering is significant. A way of decreasing light scattering is to decrease the size of the miniemulsion droplets using efficient homogenization devices [45,46]. It is worth mentioning that microemulsion, as a transparent system, could be advantageous for photoinduced reactions, but unfortunately it cannot be used to synthesize polymer hybrids. A way to overcome the limitations in the penetration depth of the light is to use a narrow continuous tubular reactor, which, in addition to the efficient light utilization, will ensure efficient heat removal. This is particularly interesting for performing the polymerization at low temperature because under these conditions the difference between the reactor temperature and that of the cooling fluid is small. To the best of our knowledge, photopolymerization in aqueous dispersed media in continuous tubular reactors has not been reported yet, although polymerization in solution has already been implemented in a narrow channel tubular reactor [47].

In this work, for the first time, hybrid latexes were produced via miniemulsion photopolymerization using a continuous tubular reactor. The hybrid was formed by simultaneous free radical

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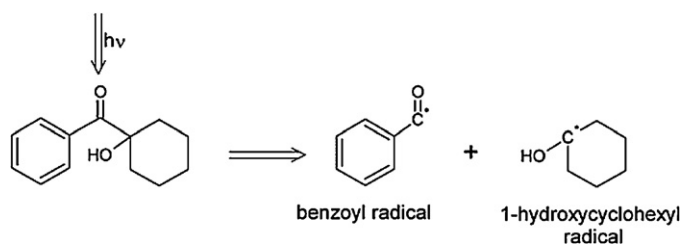


Fig. 1. Photolysis of the molecule of 1-hydroxycyclohexyl phenyl ketone (HCPK).

polymerization and addition polymerization. UV light was used to initiate the free radical polymerization of acrylic monomers using an oil-soluble photoinitiator (PI). The addition reaction of the isocyanate groups of the PU with the hydroxyl groups of the acrylic monomers, which is not sensitive to UV light, was catalyzed with dibutyltin dilaurate (DBTDL). It is shown that the initiation conditions are powerful tools to modify the microstructure of these complex materials, opening new possibilities in the design of these polymers.

## 2. Experimental part

### 2.1. Materials

Technical grade monomers, 2-ethylhexyl acrylate (2-EHA, Quimidroga), methyl methacrylate (MMA, Quimidroga), methacrylic acid (MAA, Aldrich) and 2-hydroxyethyl methacrylate (HEMA, Fluka), were used as received. A long chain *n*-octadecyl acrylate (SA, Aldrich) was utilized as a reactive costabilizer in order to prevent Ostwald ripening [10]. A polyether and aliphatic isocyanate terminated PU prepolymer, Incorez 701 (PU) (Incorez Ltd.) specially designed for adhesive applications, was used without further purification. The equivalent weight of the prepolymer is 1050 g/equivalent and the NCO concentration is ca. 4 mol%. Because of the low molecular weight (3285 g/mol) of Incorez 701, Bisphenol A (BPA, Aldrich) was used as chain extender. Dibutyltin dilaurate (Aldrich) was utilized as polyaddition catalyst without any purification. Dowfax 2A1, (alkyl diphenyloxide disulfonate, Dow Chemicals) was used as surfactant to prepare the miniemulsions and sodium dodecyl sulphate (SDS, Aldrich) was added after the miniemulsification to improve the miniemulsion stability. Both were used as received. The non-bleaching oil soluble photoinitiator 1-hydroxycyclohexyl phenyl ketone (HCPK, Fig. 1, Aldrich) was used as a buffer and gel-permeation-chromatography grade tetrahydrofuran (THF, Scharlau) as a solvent. Oxygen-free

grade nitrogen was used for purging the feed. Double deionized water was used throughout this study.

### 2.2. Miniemulsification

20 wt% solid content miniemulsions were prepared as follows. First, the organic phase was prepared by dissolving the Incorez 701 (10 wt% weight based on the organic phase, wbp), BPA (amount needed for OH/NCO=2) in the monomer mixture (2EHA/SA/MMA/MAA/HEMA, 91.5/5.8/1.4/0.9/0.4 wt/wt). HCPK (0.09, 0.24 or 0.48 wt%, weight based on monomer, wbm) was also dissolved in the organic phase. Then, the organic phase was mixed with an aqueous solution of the surfactant (2 wt% wbp of Dowfax 2A1) and NaHCO<sub>3</sub> (0.02 M) under intensive magnetic stirring (15 min at 1000 rpm) to create an emulsion. The resulting coarse emulsion was sonicated for 15 min at 9 output control and 80% duty cycle with a Branson 450 instrument (Danbury, CT). Finally, in order to improve the miniemulsion stability, 1 wt% (wbm) SDS was added. After the addition, the miniemulsion was agitated for 15 min. The droplet size measured by dynamic light scattering (see below) was 180 nm.

### 2.3. Photopolymerization

The experiments were performed in a narrow continuous tubular reactor. The experimental setup is presented in Fig. 2. The reactor is composed of 15 quartz tubes connected with each other with 14 semicircular silicone bends with 2 mm inner diameter. Each quartz tube has 400 mm length, 1 mm inner diameter and 3 mm outer diameter. The total length of the reactor was 6.35 m. A UV chamber (model BS 03, Dr. Gröbel UV-Elektronik GmbH) equipped with 20 UV lamps (wavelength range from 315 to 400 nm with a maximum intensity at 368 nm) was used. The incident light irradiance (ILI) was measured using a radiometer UV sensor (which is part of the chamber) and it was varied in the range 2.5–7 mW/cm<sup>2</sup>. A gear pump (model 305, Gilson) was utilized to control the miniemulsion flow rate (0.42–4.2 mL/min). All runs were carried out under laminar conditions ( $Re \leq 61$ ) (Table 1). The miniemulsion was placed in the Erlenmeyer flask and mixed with a magnetic stirrer at 450 rpm. Prior to be fed to the reactor, the miniemulsion was purged with nitrogen for about 30 min. The measurements reported were obtained under steady-state conditions. The heat of polymerization was removed by natural convection. The reaction temperature was measured at the inlet and at the outlet of the reactor and it was almost the same (~25 °C) in both places, probably as a result of small diameter of the tubes and the solids content (20%) used. It was observed that without UV irradiation, no polymerization of monomer took place even in the presence of

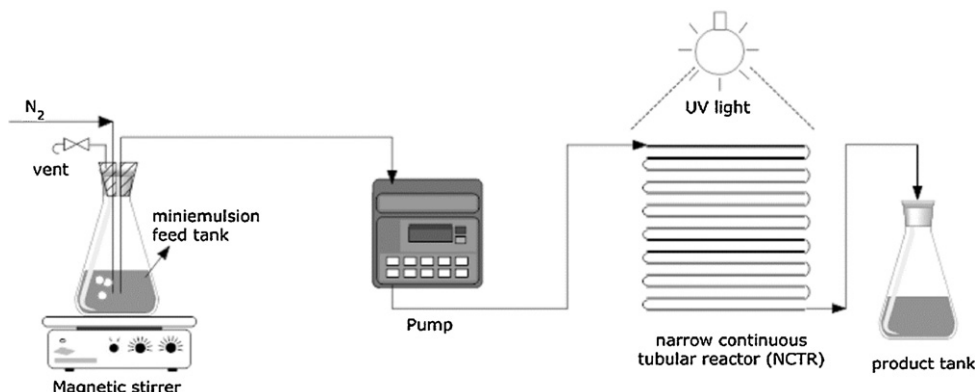


Fig. 2. Illustration of the experimental setup.

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