



## Combining SEC & MALDI for characterization of the continuous phase in dispersion polymerization



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### ABSTRACT

Dispersion copolymerization of styrene (St) with either acrylonitrile (AN) or methyl methacrylate (MMA) in 1-propanol/deionized water medium were carried out using Bisomer S20W (polyethylene oxide macromonomer with a methacrylic end group) as stabilizer. The serums of the St/AN and St/MMA latexes were characterized in terms of molar mass and composition by the combination of Size Exclusion Chromatography (SEC) and Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS). This work demonstrates that the combination of SEC and MALDI techniques is necessary for an accurate identification of the composition and molar mass of the oligomeric species present in the continuous phase of a dispersion polymerization that cannot be achieved by using either SEC or MALDI alone. For the particular latexes analyzed in this work it was found that unreacted macromonomer was present in both copolymer systems. However, in the case of the copolymerization with AN besides the presence of the macromonomer there were also some pAN oligomers.

### 1. Introduction

Dispersion polymerization is one of the most attractive heterogeneous polymerization techniques to synthesize nano- and micro-particles, since it allows the synthesis of particles with narrow and broad size distributions from a single polymerization step. Dispersions of latex particles in polar and non-polar solvents are important materials in several areas, such as coatings, materials for electroforetic displays [1,2], toners [3], column packing materials for chromatography [4], printing plates for lithography [5], spacers for liquid crystal displays, and sensors for biomedical and biochemical analysis [4,6,7].

In dispersion polymerization, the monomer(s) and the stabilizer are dissolved in the solvent mixture to form a homogeneous solution (Scheme 1A). After the addition of initiator, polymerization proceeds as a solution polymerization (Scheme 1B). The solubility of the oligomeric radicals formed is dependent on the chain length, composition, and the solvency of the medium [8]. Once the reaction medium is selected to be a good solvent for monomer, initiator and stabilizer, but a poor solvent for the polymer produced, the polymer chains will precipitate from the

medium once they exceed a critical chain length ( $j_{cr}$ ) (Scheme 1C). The precipitated polymer chains will form nuclei, which can grow by polymerization or aggregation with each other to form mature particles with subsequent adsorption of stabilizer (Scheme 1D). Thereafter, no further nucleation occurs, and the particle size increases (by transfer of monomer from the continuous phase) until the monomer is consumed (Scheme 1E) [6,8–10].

Several types of stabilizers have been used in dispersion polymerization. Croucher and Winnik [11] classified in three types the polymers which have been successfully used as steric stabilizers in organic phase dispersion polymerization:

- Random or block copolymers [12]. Really effective and they are synthesized in a previous step of the dispersion polymerization reaction.
- Homopolymers [6,8,13–18]. Initially they are soluble on the reaction medium. The most used homopolymers are: polyvinylpyrrolidone (PVP) [17,19–25], hydroxypropylcellulose (HPC) [21,26–31], polyacrylic acid (PAA) [19,21,32–35] and polyvinyl

**Abbreviations:** MALDI, Matrix Assisted Laser Desorption Ionization; TOF, Time of Flight; MS, Mass Spectrometry; MMD, molar mass distribution; SEC/RI, Size Exclusion Chromatography/Refractive index; St, styrene; AN, acrylonitrile; MMA, methyl methacrylic acid; EO, ethylene oxide; AIBN, azobisisobutyronitrile; THF, tetrahydrofuran; CHCA,  $\alpha$ -cyano-4-hydroxycinnamic acid; NaTFA, sodium trifluoroacetate

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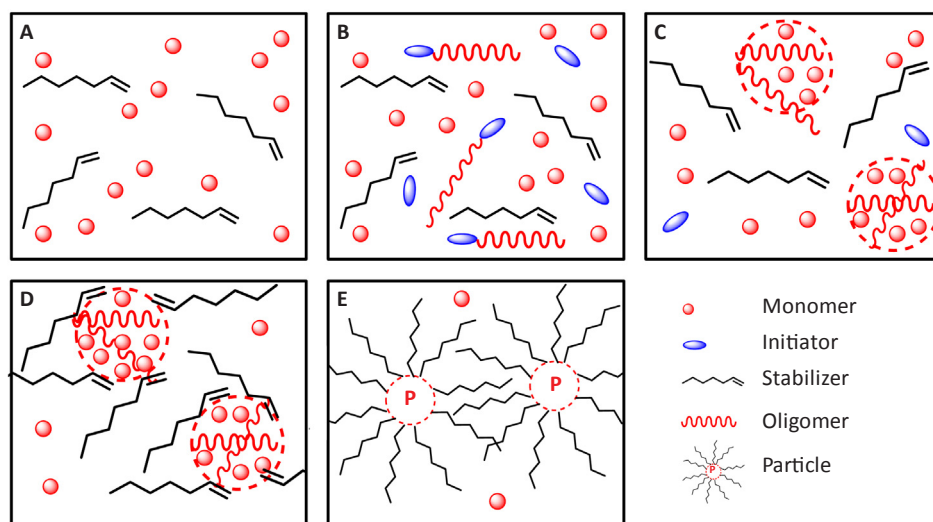
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Scheme 1. General mechanism for dispersion polymerization.

alcohol (PVA) [36–40].

(c) Macromonomers [10,12,41–46]. Macromonomers are low molar mass polymeric species that contain a polymerizable end-group which can be copolymerized with the monomers to produce polymer particles with the stabilizer covalently bounded to the surface of the formed polymer particles.

However, besides the stabilizer type and concentration there are many other variables that affect the dispersion polymerization process and have been deeply studied such as, the type and concentration of the comonomer and the medium composition. Yand et al. [45] observed that by copolymerizing styrene with different vinyl monomers in polar solvents the particle size increased as the concentration of the hydrophilic comonomer increased. On the other hand, Jiang et al. [9] studied the effect of the medium composition (monomer and solvent) and they observed that methyl methacrylate (MMA) monomer concentration decreased linearly in both phases (particles and continuous phase) whereas the MMA ratio between particles and continuous phase kept constant but favouring the presence in the continuous phase.

Most of the works carried out to understand the kinetics of the polymerization and nucleation mechanism in dispersion polymerization are related to the study of stabilizer type and concentration, continuous phase composition and type of comonomer [43–45].

An important aspect of dispersion polymerization is the formation of polymers in the continuous phase which do not reach the critical length to form a nuclei and as a consequence they remain in the continuous phase or eventually they can be adsorbed in the polymer particles. The continuous phase, also known as the serum, is referred to the liquid phase where the particles are dispersed. Depending on the system or the polymerization process the composition of the serum can be very complex and many different species, such as, stabilizer, residual monomer, short chain polymers (oligomers)... can be found. The characterization of the serum composition can yield very interesting and valuable information that may help understanding the polymerization process and/or explaining the differences observed between different systems. In spite of the importance of the composition of the serum in the nucleation mechanism, there are few works reporting the characterization of the serum [47,48]. Moreover, the lack of this type of analysis is a drawback for the assessment of mathematical models developed for the copolymerization of sparingly water soluble and water soluble monomers in (mini)emulsion polymerization [47–50].

In the present work two different latexes, styrene-co-acrylonitrile and styrene-co-methyl methacrylate were synthesized by dispersion polymerization in 1-propanol/distilled deionized (DDI) water medium

and using a polyethylene oxide macromonomer with a methacrylic end group (Bisomer S20W) as stabilizer.

The aim of this work was to assess the combination of Size Exclusion Chromatography (SEC) and Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) techniques to characterize the species present in the continuous phase of the dispersion polymerization medium. This was done in the serum of the two final latexes synthesized in this work with the objective of extending this analysis in a follow up work to the initial stages of the polymerization to shed light on the complex mechanisms of nucleation in dispersion polymerization. The article is organized as follows: first the experimental details regarding the synthesis of the two latexes and the SEC and MALDI-TOF equipments are discussed. Then the limitations of the SEC technique used alone to characterize the oligomeric species of the serum are presented. The analysis of the serums by MALDI-TOF although provides further insight on the composition of the species is not enough, and coupled SEC/MALDI-TOF by injection of selected fractions of the serum obtained by SEC in the MALDI-TOF equipment are presented and discussed in detail for both copolymer latexes. Finally, the composition of the serums of both latexes is presented.

## 2. Experimental section

### 2.1. Materials

Styrene (St) (from Quimidroga), methyl methacrylate (MMA) and acrylonitrile (AN) monomers were used as received (from Aldrich) without further purification. 2,2'-azobisisobutyronitrile (AIBN, Aldrich) was the thermal initiator and it was stored at 4 °C before its use. Deionized water (DDI) and 1-propanol (nPA) (Aldrich) were used as a continuous phase of the polymerization. Polyethylene oxide macromonomer (MPEGMA, Bisomer S20W, Cognis, ~45 ethylene oxide units,  $M_w = 2600 \text{ g mol}^{-1}$ ) was used as stabilizer.

### 2.2. Synthesis of *p*(St-co-AN) and/or *p*(St-co-MMA) by dispersion polymerization

A typical polymerization was carried out following this procedure: In a 1L jacketed reactor 61.24 g MPEGMA were dissolved in a mixture of water and 1-propanol (68.74 g and 390 g, respectively). Then, 30 g of St and 100 g of AN (or MMA) were added and the mixture was heated to 75 °C under nitrogen atmosphere and constant stirring (200 rpm). After heating for 30 min, 1g of 2,2 azobisisobutyronitrile (AIBN) dissolved in nPA at 1.54 wbm and heated at the same temperature, was added into

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