

# EVOLUTION OF POLYMER PARTICLE SIZE AND MOLECULAR WEIGHTS IN SEMICONTINUOUS EMULSION COPOLYMERIZATION OF ACRYLIC MONOMERS

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Emulsion polymerization is a heterogeneous polymerization process involving the polymerization of organic monomers with very limited solubility in water by free radical reactions. The product is a latex consisting of sub-micron polymer particles dispersed in water. Free radicals are compartmentalized in the particles giving rise to high molecular weights and polymerization rates. The latexes are used in applications such as coatings, adhesives, high impact polymers, additives for construction materials, and in many other high-value-added products in areas such as membrane separation, biomedical and biotechnology.

The control of the variables governing the copolymerization process allows the production of a wide range of polymer microstructures as well as colloidal formulations [1]. Among these variables are the comonomers ratio, temperature, initiator concentration, monomer addition policies, presence of surfactants, etc.

In this work we study the effect of initiator, temperature and monomers feeding time in the emulsion polymerization of butyl methacrylate (BMA) and styrene (S) on the particle size and molecular weights distribution of the resulting latexes. Reactions were carried out in a LABMAX<sup>®</sup> automated reactor equipped with two controlled feeding lines, one for the monomers and the other for water, initiator and emulsifier. Particle sizes were measured by dynamic light scattering (Z sizer 3000 HS); this technique provides the z-average mean size ( $D_z$ ). Molecular weight distributions (MWD) were determined by means of size-exclusion chromatography (SEC) system which consisted of a Waters 510 HPLC pump, a Rheodyne 7725i manual injector, a Waters model 410 differential refractive index (RI) detector, and a Viscotec TriSEC<sup>®</sup> model 270 dual detector. Data collection and analysis was performed with TriSEC<sup>®</sup> GPC software.

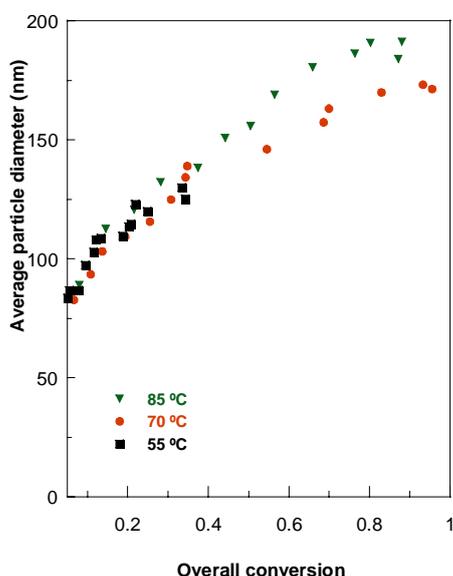


Figure 1. Effect of the reaction temperature on the particle size.

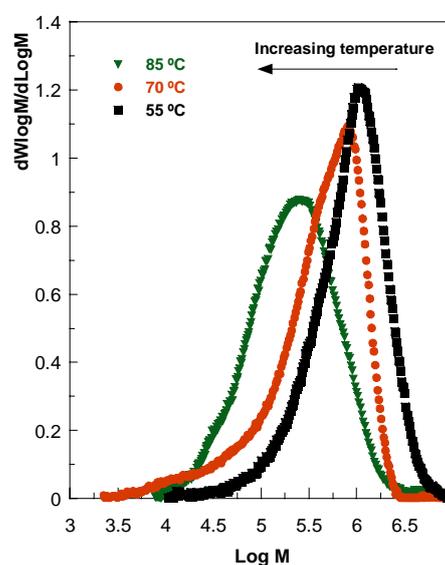


Figure 2. Effect of the reaction temperature on MWD.

Figures 1 and 2. show the effect of temperature on the average particle size and molecular weight distribution, respectively, for the seeded copolymerization of BMA/S with a 50:50 weight ratio using a feeding time of 4 h and an initiator ( $K_2S_2O_8$ ) content of 0.27% referred to the monomer. It can be that the average particle size increases with conversion starting from about 80 nm for the seed to 170-190 nm at the end of the reaction. The effect of temperature is not very important; the slight increase that can be observed at 85°C is due to a lack of colloidal stability leading to polymeric particles coagulation. In contrast the influence of temperature in the molecular weight distributions is very relevant, as illustrated in Figure 2. The maximum of the distributions corresponds to the weight average molecular weight ( $\overline{M}_W$ ). As temperature increases the overall distribution shifts to lower molecular weights, which is a typical behaviour in polymerizations using thermal initiators [2], as in our case. Mechanical, rheological and adhesive polymer properties are very dependent on the molecular weight. For example, in the case of pressure contact adhesives, the shear resistance increases with molecular weight, whereas the tack and peel resistances show optimum values at intermediate molecular weights. On the other hand, the particle size is more important in all the aspects concerning the surface properties.

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#### **References:**

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- [2] A. D'Anjou, J. Torrealdea, J.R. Leiza, J.M. Asua, G. Arzamendi, Macromolecular Theory and Simulations, **12** (2003) 42.