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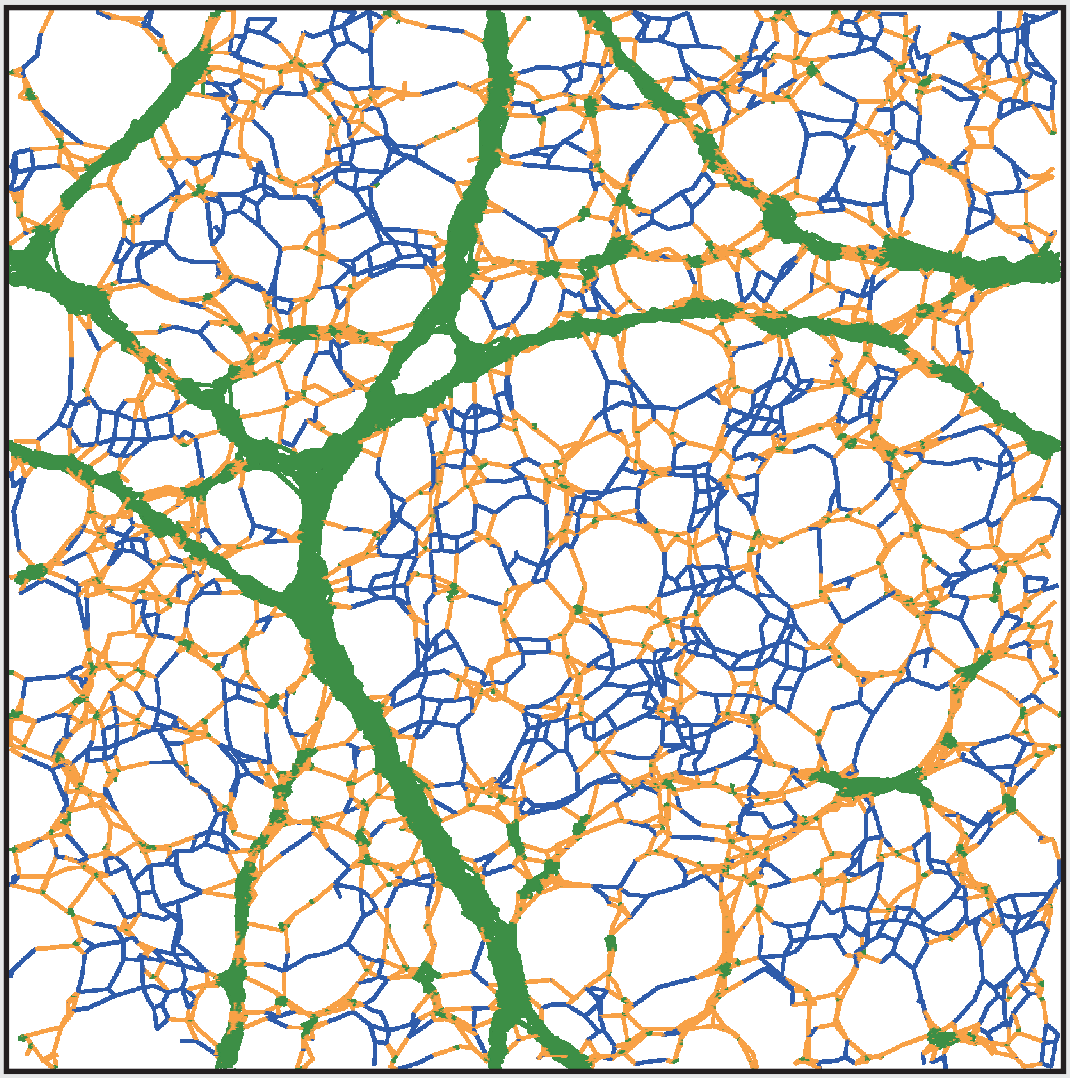
Program and Abstracts



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Kinetic Modeling of the Inverse Suspension Production of Acrylic Gels using *In-Line* FTIR-ATR Monitoring and *Off-Line* SEC/RI/MALLS Product Characterization

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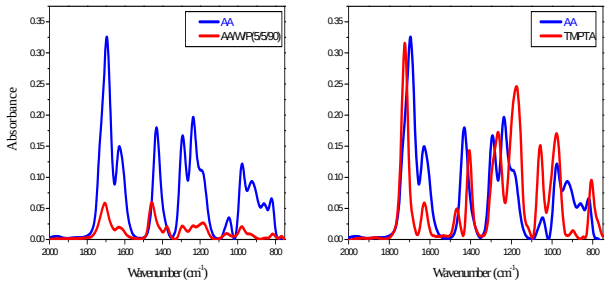
This work describes the production of acrylic gels in a batch stirred reactor at 1.5 dm^3 scale. Inverse suspension technique is used within this purpose. Paraffin (P) was used in the continuous phase and polymer networks were synthesized in the dispersed phase containing water (W) dissolved acrylic acid (AA), trimethylolpropane triacrylate (TMPTA), used as crosslinker, and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V50) as a free radical initiator.

The influence of key parameters in the network formation, namely reaction temperature and pH, is investigated. Different experiments have been performed in the temperature range 20 to 60 °C. The aqueous phase containing the monomers was neutralized using sodium hydroxide in order to obtain a predefined pH level. Polymerizations have been conducted at different pH values, in the range 3 to 5, and the influence of this parameter in monomers consumption is assessed.

These polymerizations are *In-Line* monitored using a FTIR-ATR immersion probe. Real time information concerning the building process of the networks is thus obtained, namely the reactivity ratios of the involved monomers. In complement to previous works [1], it is expected that important additional details such as the reactivity of pendant double bonds of TMPTA can also be evaluated.



(a) (b)

Figure 1 (a) FTIR-ATR spectra of pure AA and an AA/W/P inverse suspension (5/5/90) showing the ability to perform the *In-Line* FTIR-ATR monitoring of such polymerization process. (b) FTIR-ATR spectra of pure AA and pure TMPTA. Spectral differences are explored to obtain real time data of the copolymerization.

Samples with different polymerization time are withdrawn from the reactor in order to obtain the dynamics of product formation. Sampling was performed before and after gelation. These samples are characterized *Off-Line* using a SEC system with simultaneous Refractive Index (RI) and Multi-Angle Laser Light Scattering (MALLS) detection. Molecular weight distribution (MWD) and correspondent averages as well as the *z*-average radius of gyration are thus measured for the soluble fraction (sol) of the synthesized non-linear polymers. Monomer conversion was estimated using these SEC traces. The weight fraction of sol in samples collected after gelation was also measured.

A general kinetic approach [2-4] is used to perform the modeling of such polymerization processes. This theoretical method can be applied before and also after gelation which is a crucial issue for the present case study. Predictions of MWD, sequence length distributions and *z*-average radius of gyration of the soluble fraction are possible within the framework of this approach. The dynamics of growth of the gel fraction could also be calculated.

A detailed kinetic model accounting for possible different reactivities of double bonds involved in the crosslinking process (pendant double bonds of TMPTA) was thus developed for acrylic/triacrylate copolymerization. Other phenomena with possible impact in the development of non-linear structures, such as chain transfer to polymer or polymerization of terminal double bonds are also included in the modeling studies.

Comparisons of the experimental results with the predictions of the developed model yield new insights in the polymer reaction engineering of acrylic gels. The relative impact of the aforementioned crosslinking/branching mechanisms in the molecular architecture of the synthesized materials and the estimate of the importance of intramolecular cyclization reactions are expected outcomes.

The design of operating conditions allowing the optimization of the end-use properties of superabsorbent acrylic gels is another long-term goal of the present research.

References

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