

## SUPPORTING MATERIAL

### EXPERIMENTAL

#### Materials

Styrene (Aldrich) was purified of inhibitor by passing through an inhibitor-removal column (Aldrich). Sodium dodecylsulfate (SDS, Fluka) and sodium peroxydisulfate (SPS, Merck) were used as received. The RAFT agent 1-(*O*-trifluoroethyl-xanthyl)ethylpropionate; F-MADIX) was synthesized according to the literature procedure<sup>1</sup>. Distilled-deionized water was used in all polymerizations.

#### Emulsion Polymerizations

The *ab initio* emulsion polymerizations were performed in a double-walled 250 ml glass reactor equipped with mechanical stirrer, condenser and thermometer. The polymerizations were carried out under nitrogen using 175 g of water, 75 g of styrene, with varying amounts of 1-(*O*-trifluoroethyl-xanthyl)ethylpropionate, SDS and SPS concentrations (see Table 1) at 70°C: Samples were taken periodically to monitor conversion, particle size distribution and molecular weight distribution. Conversion was determined by gravimetric analysis.

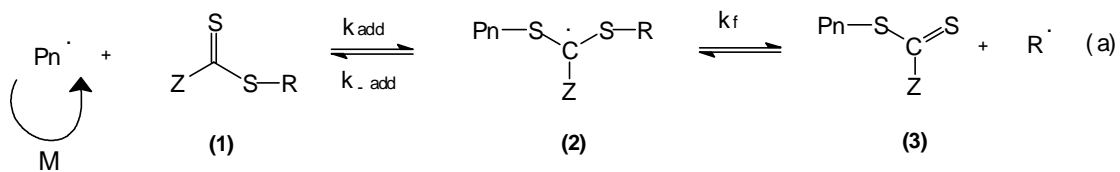
### **Capillary Hydrodynamic Fractionation (CHDF)**

The particle size distribution and number-average diameter of the latex particles were determined by capillary hydrodynamic fractionation techniques (CHDF 2000 2.73, Matec Applied Sciences).

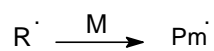
### **Size Exclusion Chromatography (SEC)**

The dried polymer was dissolved in tetrahydrofuran (THF, Biosolve) to a concentration of 1 mg/mL. The solution was filtered over a 0.2 mm PTFE syringe-filter. Analysis was carried out using a Waters model 510 pump, a Waters model WISP 712 auto-injector, a model 410 refractive index detector, and a model 486 UV detector (at 254 nm). The columns used were a PLgel guard (5  $\mu$ m particles) 50  $\times$  7.5 mm pre-column, followed by two PLgel mixed-C (5  $\mu$ m particles) 300  $\times$  7.5 mm columns in series (which were maintained at 40 °C for analysis). The columns used separate polymers in the molecular weight range between 500 to 2 million with high resolution. THF was used as an eluent (flow rate 1.0 mL/min), and calibration was done using polystyrene standards (Polymer Laboratories;  $M = 580 - 7.1 \times 10^6$ ). Data acquisition was performed using waters Millenium 32 (v3.05) software.

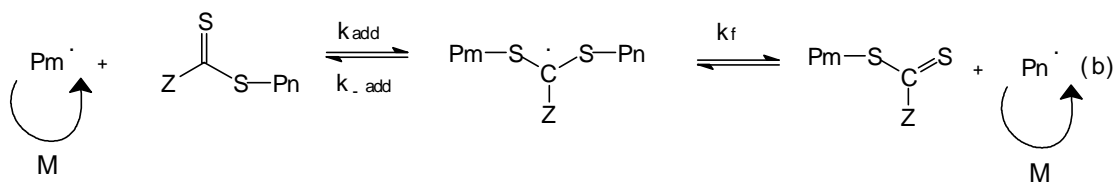
### Chain Transfer



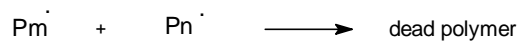
### Reinitiation and Propagation



### Chain Equilibrium



### Termination



Scheme 1: The mechanism of the reversible addition-fragmentation chain transfer

(RAFT) polymerization.

d vs conversion (particle)

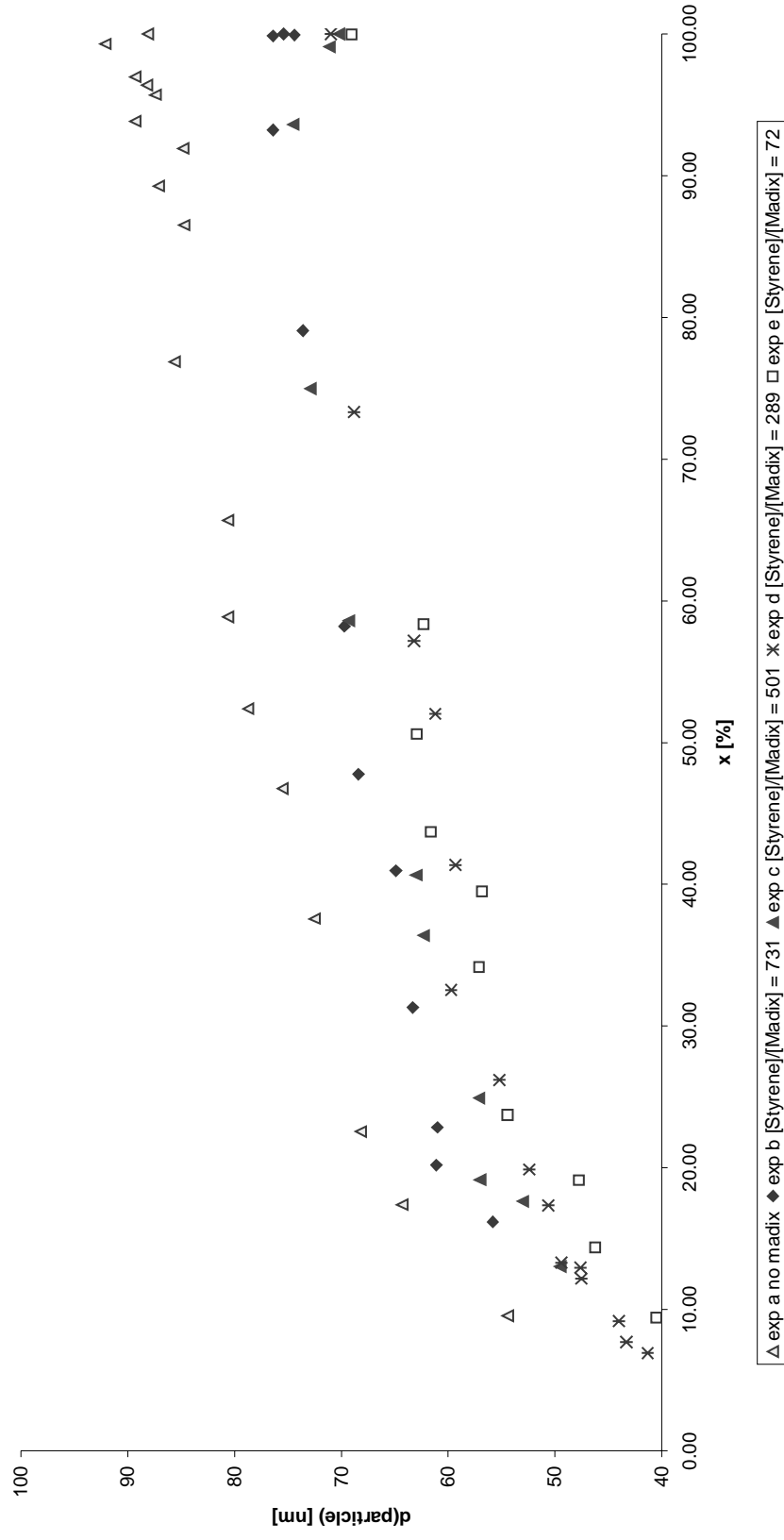


Figure 1. Evolution of the number-average diameter,  $d_p$ , with conversion at a concentration of SPS of  $0.01 \text{ mol} \cdot \text{dm}^{-3}$  and SDS of  $1.5 \text{ mol} \cdot \text{dm}^{-3}$  at different F-MADIX concentrations. The measurements were done by capillary hydrodynamic fractionation (CHDF).

### Calculation of $\bar{n}$ during Interval II

$\bar{n}$  was calculated using the following equation<sup>2</sup>:

$$\frac{dx}{dt} = \frac{k_p C_p N_c}{n_M^0 N_A} \bar{n} \quad (1)$$

Where  $k_p$  is the rate constant for propagation,  $C_p$  is the concentration in the particles during Interval II (taken as 5.6 M),  $N_c$  is the number of particles per unit volume,  $n_M^0$  is the initial moles of monomer and  $N_A$  is Avogadro's number.  $N_c$  was calculated from the number average diameter (Table 1 in manuscript and Figure 1 above). The rate,  $dx/dt$ , was calculated from the slopes in Figure 2.

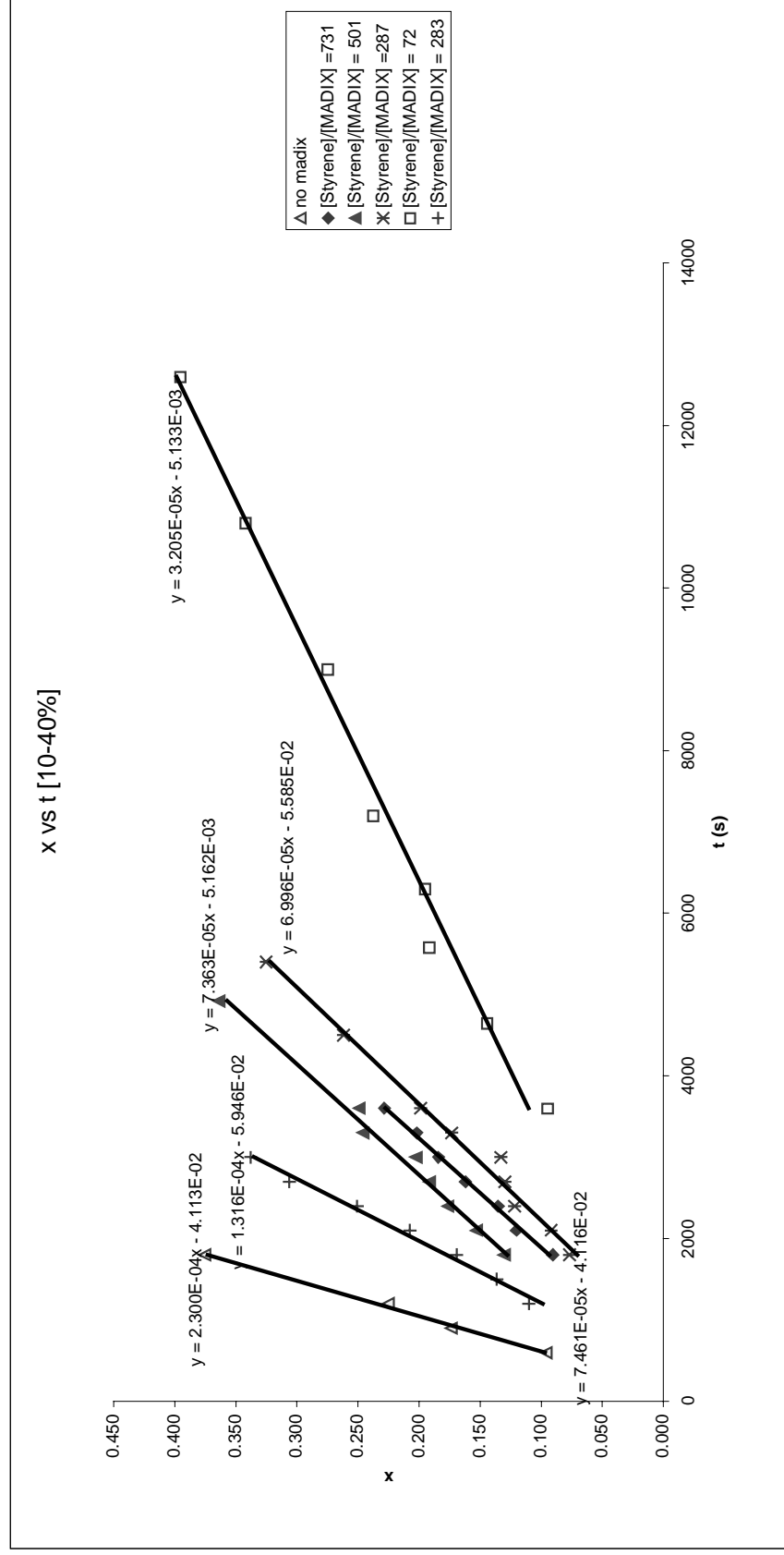


Figure 2. Conversion-time profile for the ab initio emulsion polymerizations of styrene carried out at a constant [SDS] of  $1.5\text{mol.dm}^{-3}$ , while varying both [MADIX] and [SPS]. The focus was on the Interval II (i.e. between approximately 10-40% conversion).  $\bar{n}$  was calculated from the slopes (see Equation 1).

**Calculation of the change in moles of F-MADIX in the particle and droplet as a function of conversion during Interval II.**

We first assume that we are dealing with a single particle where monomer is converted to polymer with an additional amount of monomer that swells this particle. The latter can be calculated from the concentration of monomer in the particle,  $C_p$ , and during Interval II is at its saturation concentration (in the case of styrene,  $C_p^{\text{sat}}$  is 5.6). Therefore, the swollen radius,  $r_s$ , is given by the following equation<sup>2</sup>.

$$r_s = \left( \frac{3}{4\pi} \frac{x g_{\text{mon}}^0}{d_{\text{poly}}} \right)^{1/3} \left( \frac{d_{\text{mon}}}{d_{\text{mon}} - C_p M_0} \right)^{1/3} \quad \dots(2)$$

Where  $x$  is conversion of monomer to polymer,  $g_{\text{mon}}^0$  is initial mass of monomer,  $d_{\text{poly}}$  is density of polystyrene (1062 g L<sup>-1</sup>),  $d_{\text{mon}}$  is density of styrene monomer (905 g L<sup>-1</sup>), and  $M_0$  is molecular weight of the monomer repeating unit (104 for styrene).

*Moles of monomer in the particle:*

$$mol_{\text{mon,part}} = \frac{(V_s - V_p) d_{\text{mon}}}{M_0} \quad \dots(3)$$

Where  $V_s$  is the swollen particle volume and  $V_p$  the unswollen volume of the particle.

*Moles of monomer in the droplet:*

$$mol_{\text{mon,drop}} = \frac{(g_{\text{mon}}^0 - g_{\text{mon,part}} - g_{\text{mon}}^0 x) d_{\text{mon}}}{M_0} \quad (4)$$

Where  $g_{\text{mon,part}}$  is the mass of monomer in the particle.

*Moles of F-MADIX in the particle and droplet:*

The moles of F-MADIX at  $x$  is given by<sup>3</sup>:

$$mol_{MADIX,x} = mol_{MADIX}^0 (1-x)^{C_{tr,RAFT}} \quad (5)$$

Where  $mol_{MADIX}^0$  is the initial moles of F-MADIX and  $C_{tr,RAFT}$  is the transfer constant for F-MADIX.

For the moles of F-MADIX to be calculated in the particle, we know that the  $M_n$  and PDI profiles fit well with solution-based simulations. Thus the ratio,  $R$ , of moles of monomer to moles of F-MADIX at  $x$  must be equivalent to  $R$  in a solution polymerization, and is given by the following relationship.

$$R = \frac{mol_{mon}^0 (1-x)}{mol_{MADIX,x}} = \frac{mol_{mon,x}}{mol_{MADIX,x}} \quad (6)$$

Therefore, the moles of F-MADIX in the particle is

$$mol_{MADIX,part} = \frac{mol_{mon,part}}{R} \quad (7)$$

and the moles of F-MADIX in the droplet is

$$mol_{MADIX,drop} = mol_{MADIX,x} - mol_{MADIX,part} \quad (8)$$



## REFERECNCES

- (1) Destarac, M.; Charmot, D.; Zard, S.; Franck, X.; Rhodia Chemie, 2000; Vol. WO 0075207.
- (2) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic: London, 1995.
- (3) Müller, A. H. E.; Zhuang, R.; Yan, D.; Litvenko, G. *Macromolecules* **1995**, 28, 4326.