Chain-growth polymerization, case study:

Solution Free Radical Polymerization (FRP) in Batch reactor

A free radical polymerization of the monomer M is carried out in a 20 L batch, isothermal and well stirred reactor, using the initiator I and a good solvent S for both the monomer and the polymer. The initial monomer concentration is M0 = 4.7 mol/L and the initiator was used with a weight fraction wI,0 = 0.01 with respect to the monomer. In order to describe the process, the chain transfers to solvent and to polymer are assumed negligible, so that the following kinetic steps can be considered:

Initiation:	$I_2 \xrightarrow{k_d, f} 2R_1^{\cdot}$
Propagation:	$R_n^{\cdot} + M \xrightarrow{k_p} R_{n+1}^{\cdot}$
Chain transfer to monomer:	$R_n^{\cdot} + M \xrightarrow{k_{fm}} P_n + R_1^{\cdot}$
Termination:	$R_n^{\cdot} + R_m^{\cdot} \xrightarrow{k_{tC}} P_{n+m}$
	$R_n^{\cdot} + R_m^{\cdot} \xrightarrow{k_{tD}} P_n + P_m$

To account for the diffusion limitations, the following expressions are available for k_p (glass effect) and k_t (gel effect):

$$k_P = \left(\frac{1}{k_{p,0}} + \frac{exp(C_\eta w_p)}{k_{pD,0}}\right)^{-1}$$

$$k_t = \left(\frac{1}{k_{t,0}} + \frac{exp(C_\eta w_p)}{k_{tD,0}}\right)^{-1} + C_{RD} k_p (1 - w_p)$$

Where w_p is the polymer weight fraction in the reaction mixture (in computing w_p, the amount of initiator can be neglected). Moreover, the following parameters can conveniently be introduced:

$$C_{fm} = \frac{k_{fm}}{k_p}$$

$$C_t = \frac{k_{td}}{k_{tc}}$$

1. Determine the instantaneous number and weight chain length distributions (CLD) at four different values of conversion (0.1, 0.4, 0.7 and 0.9) as well as the number average, DP_N^{Inst}, and weight average, DP_W^{Inst}, degrees of polymerization with the corresponding instantaneous polydispersity. Moreover, calculate the instantaneous number average, M_n^{Inst}, and weight average, M_w^{Inst}, molecular weights in the case of:
    a) Dominant termination by disproportionation (C_{fm}=0,C_t=1000);
    b) Dominant termination by combination (C_{fm}=0,C_t=0.001);
    c) Dominant chain transfer to monomer and negligible termination by combination (C_{fm}=0.01,C_t=1000);
2. Compare the results obtained at point 1 with those obtained neglecting the diffusion limitations in the same conditions.

Starting conditions:

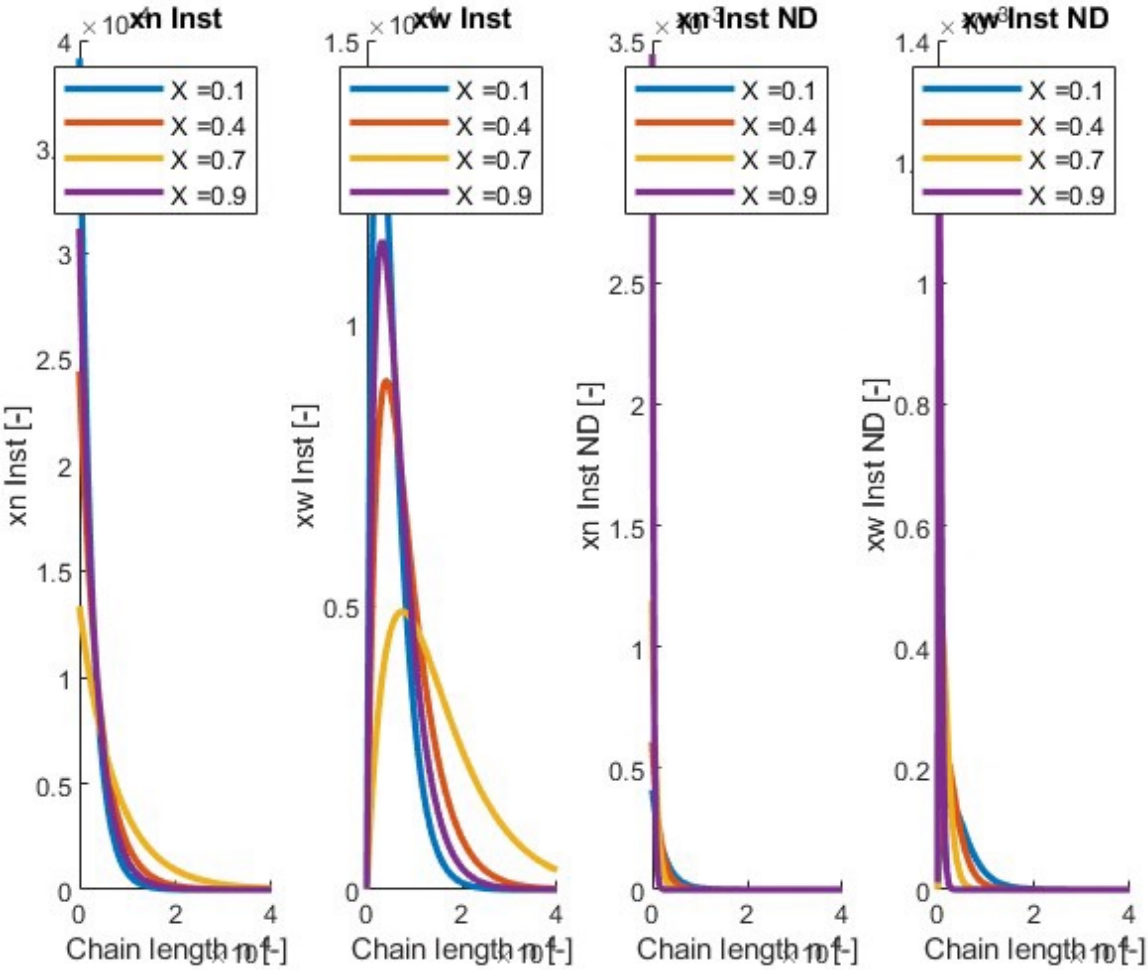
$MW_M = 100\ [g\ mol^{-1}]$ $MW_S = 78\ [g\ mol^{-1}]$ $MW_I = 164\ [g\ mol^{-1}]$

$\rho_M = 0.94\ [kg\ L^{-1}]$ $\rho_S = 0.88\ [kg\ L^{-1}]$

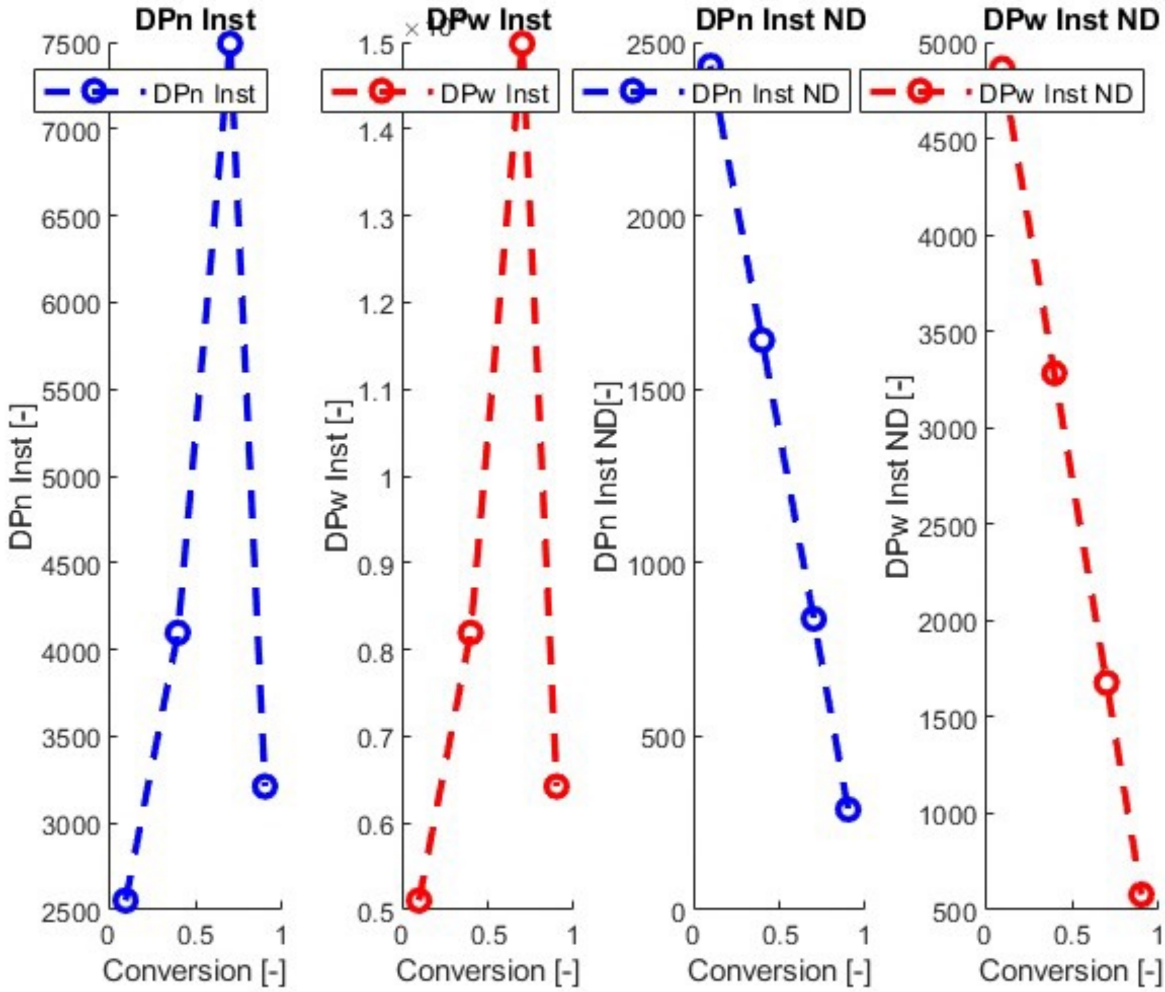
$f = 0.5\ [-]$ $k_d = 5.55\ 10^{-6}\ [s^{-1}]$ $k_{p,0} = 715\ [L\ mol^{-1} s^{-1}]$

$k_{t,0} = 9.8\ 10^6\ [L\ mol^{-1} s^{-1}]$ $k_{pD,0} = 3\ 10^{11} [L\ mol^{-1} s^{-1}]$ $k_{tD,0} = 3\ 10^8\ [L\ mol^{-1}\ s^{-1}]$

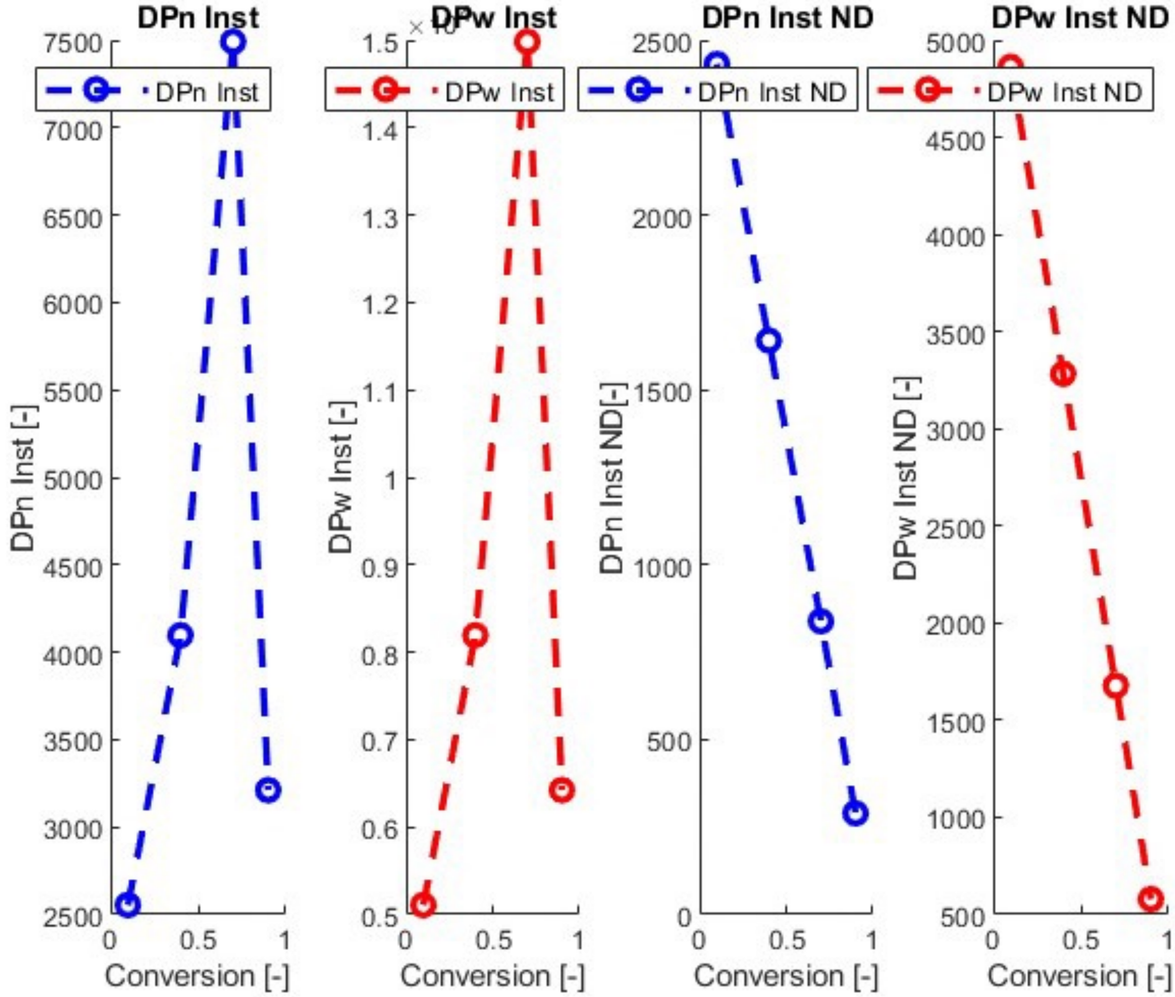
$C_\eta = 25\ [-]$ $C_{RD} = 180\ [-]$



xn Inst
xw Inst
xn Inst ND
xw Inst ND
X =0.1
X =0.4
X =0.7
X =0.9
xn Inst [-]
xw Inst [-]
xn Inst ND [-]
xw Inst ND [-]
Chain length m [-]

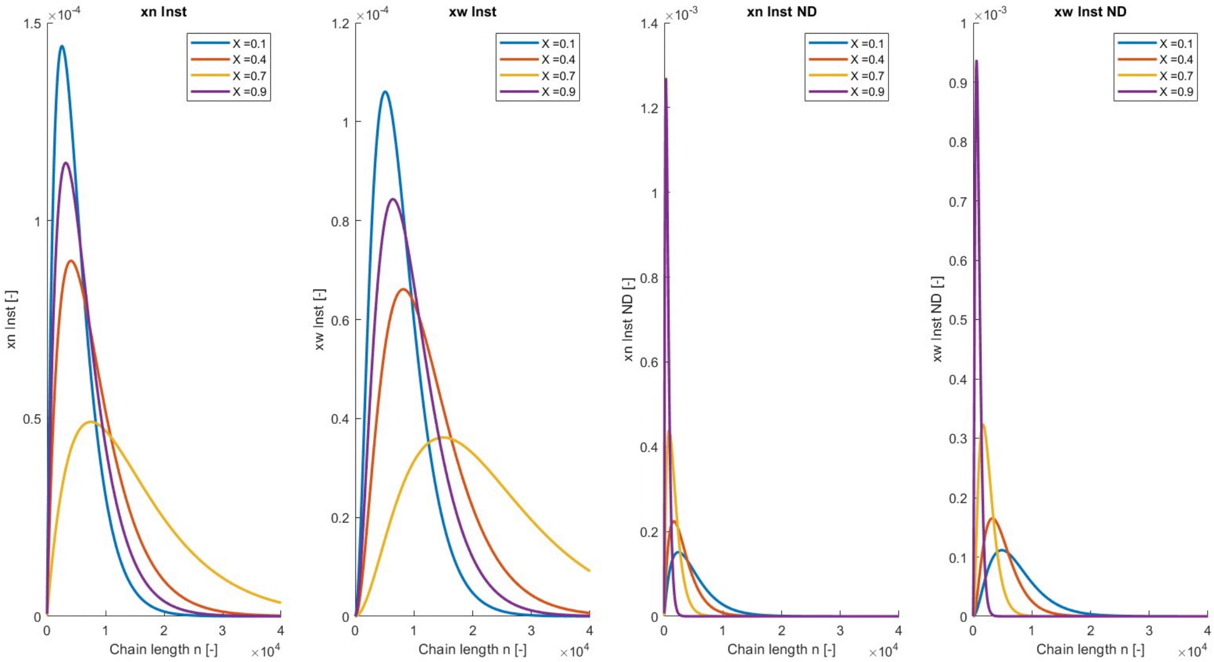


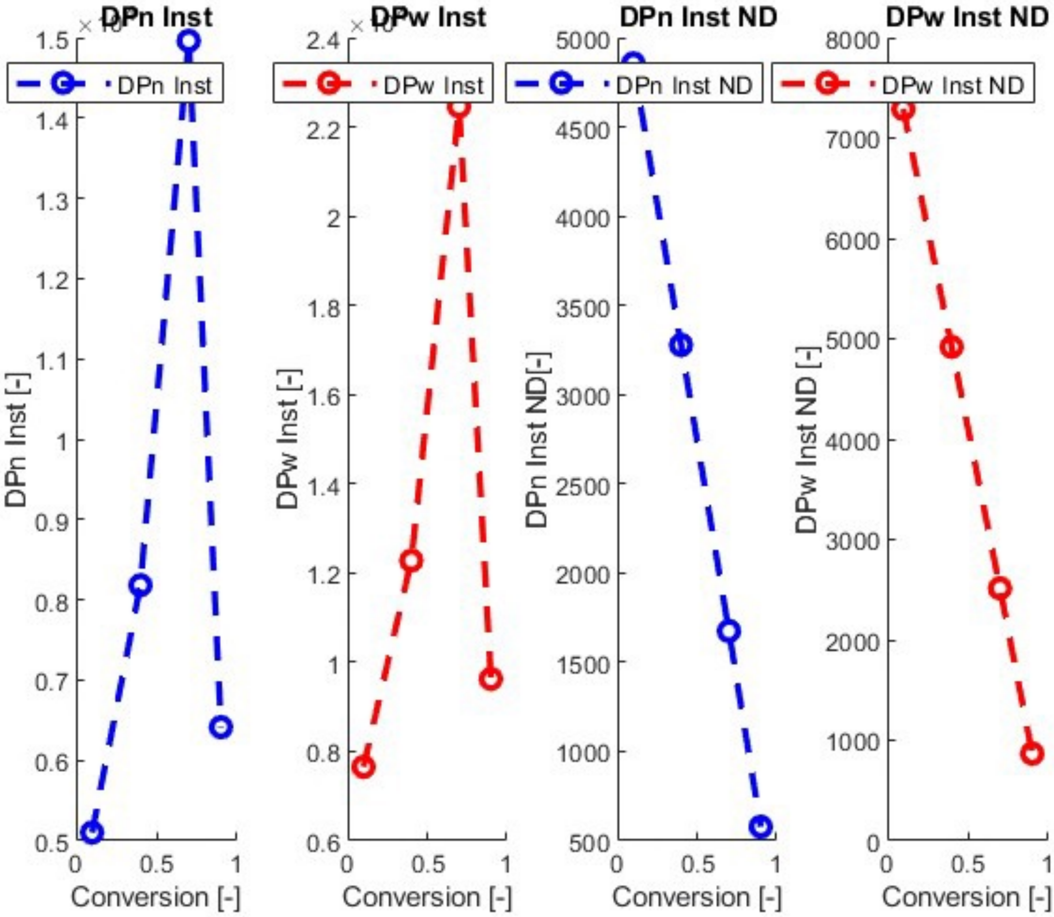
We form a lot of chains with low molecular weight



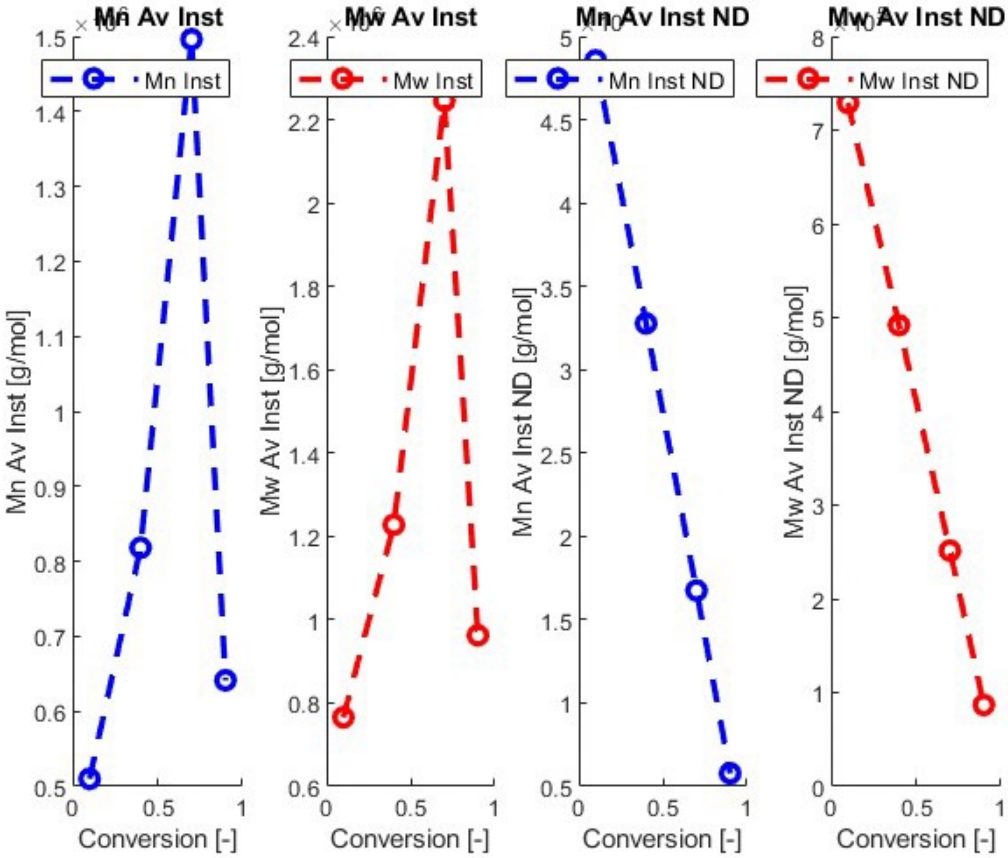
DPn Inst
DPn Inst [-]
DPn Inst
Conversion [-]
DPw Inst
DPw Inst [-]
DPw Inst
Conversion [-]
DPn Inst ND
DPn Inst ND[-]
DPn Inst ND
Conversion [-]
DPw Inst ND
DPw Inst ND [-]
DPw Inst ND
Conversion [-]

CASE 1B COMBINATION

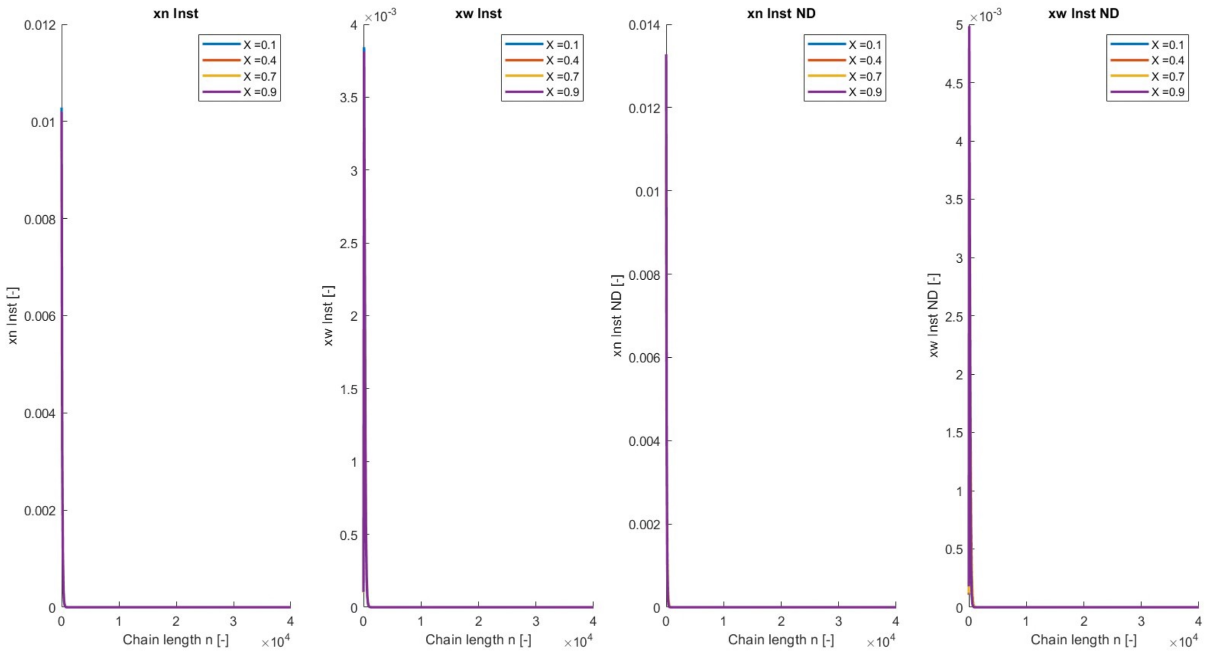




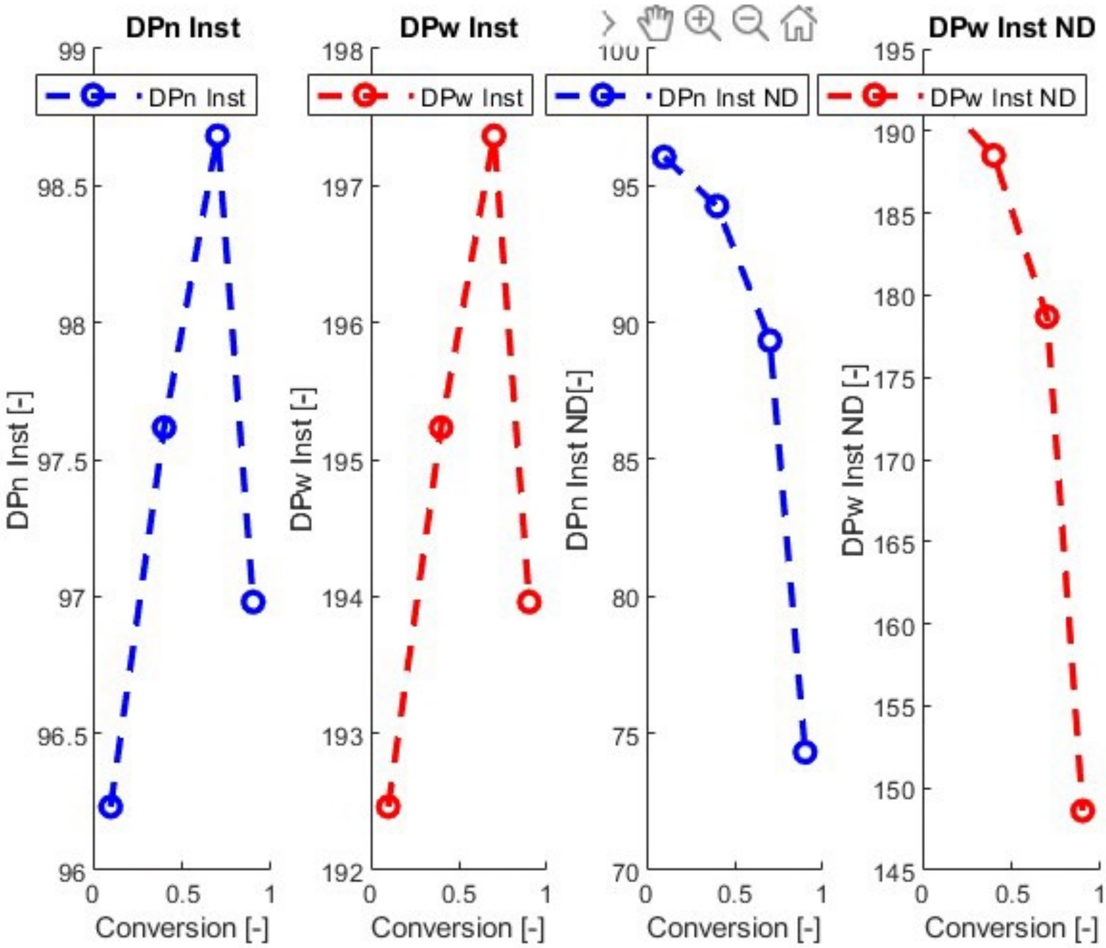
DPn Inst
DPn Inst
DPn Inst [-]
Conversion [-]
DPw Inst
DPw Inst
DPw Inst [-]
Conversion [-]
DPn Inst ND
DPn Inst ND
DPn Inst ND[-]
Conversion [-]
DPw Inst ND
DPw Inst ND
DPw Inst ND [-]
Conversion [-]



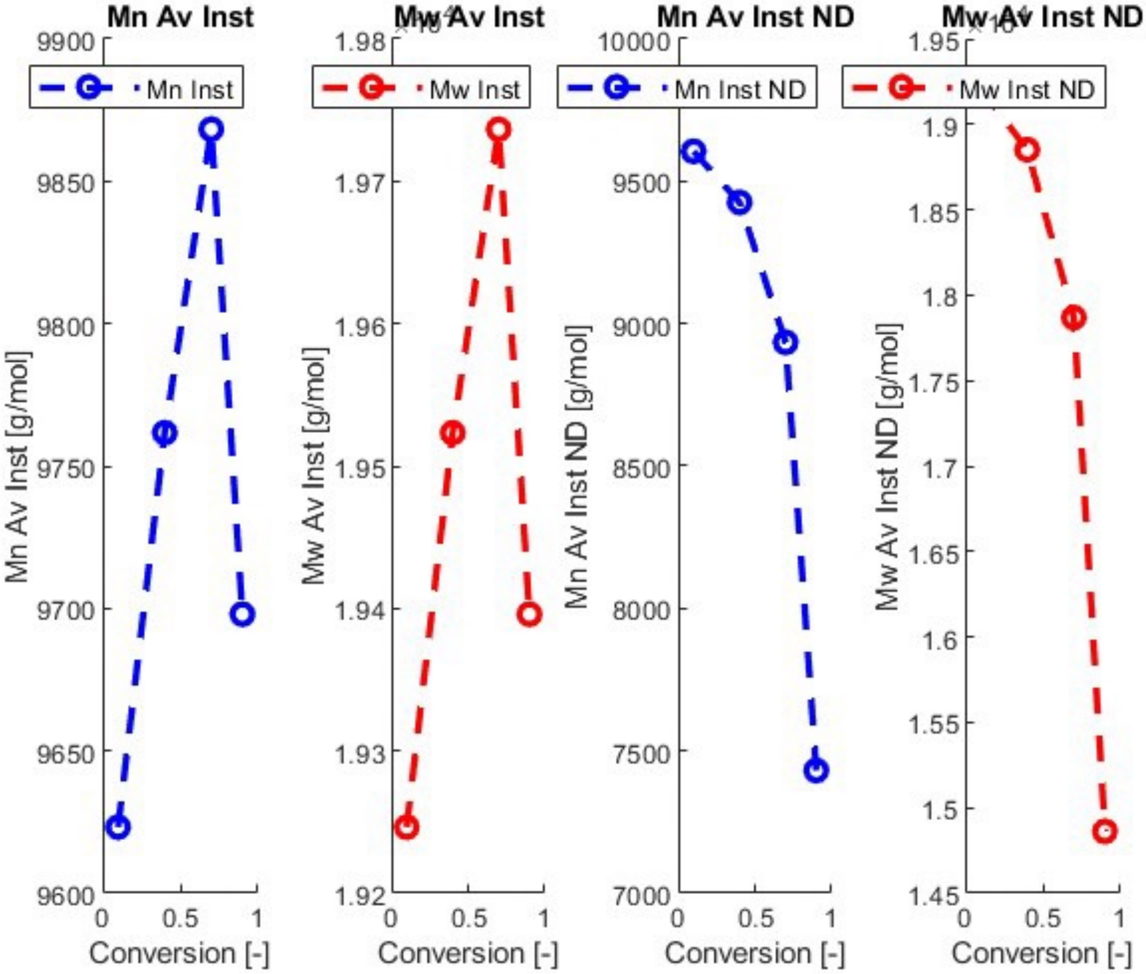
Mn Av Inst
Mw Av Inst
Mn Av Inst ND
Mw Av Inst ND
Mn Inst
Mw Inst
Mn Inst ND
Mw Inst ND
Mn Av Inst [g/mol]
Mw Av Inst [g/mol]
Mn Av Inst ND [g/mol]
Mw Av Inst ND [g/mol]
Conversion [-]
Conversion [-]
Conversion [-]
Conversion [-]



xn Inst
xn Inst [-]
0.012
0.01
0.008
0.006
0.004
0.002
0
X =0.1
X =0.4
X =0.7
X =0.9
Chain length n [-]
×10^4
xw Inst
xw Inst [-]
×10^-3
xn Inst ND
xn Inst ND [-]
0.014
xw Inst ND
xw Inst ND [-]



DPn Inst
DPn Inst
DPn Inst [-]
Conversion [-]
DPw Inst
DPw Inst
DPw Inst [-]
Conversion [-]
DPn Inst ND
DPn Inst ND[-]
Conversion [-]
DPw Inst ND
DPw Inst ND
DPw Inst ND [-]
Conversion [-]


Mn Av Inst
Mn Inst
Mn Av Inst [g/mol]
Conversion [-]
Mw Av Inst
Mw Inst
Mw Av Inst [g/mol]
Conversion [-]
Mn Av Inst ND
Mn Inst ND
Mn Av Inst ND [g/mol]
Conversion [-]
Mw Av Inst ND
Mw Inst ND
Mw Av Inst ND [g/mol]
Conversion [-]