



THE EFFECT OF PRESSURE PULSES ON CRYSTALLIZATION OF i-PP: A DILATOMETRIC STUDY

POLITECNICO
MILANO 1863

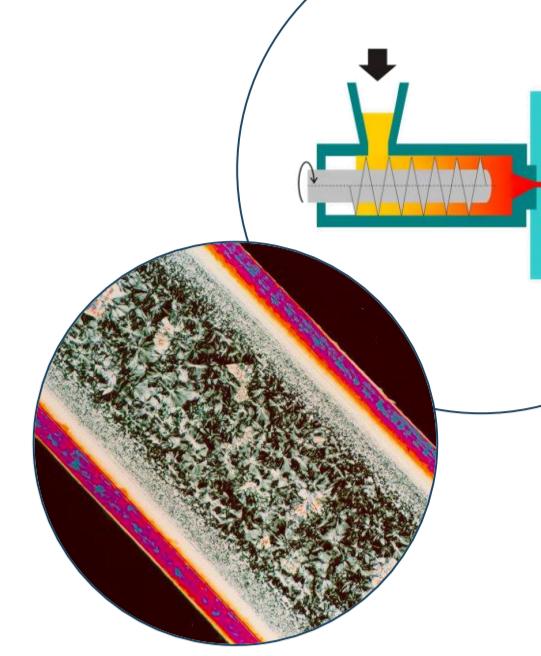
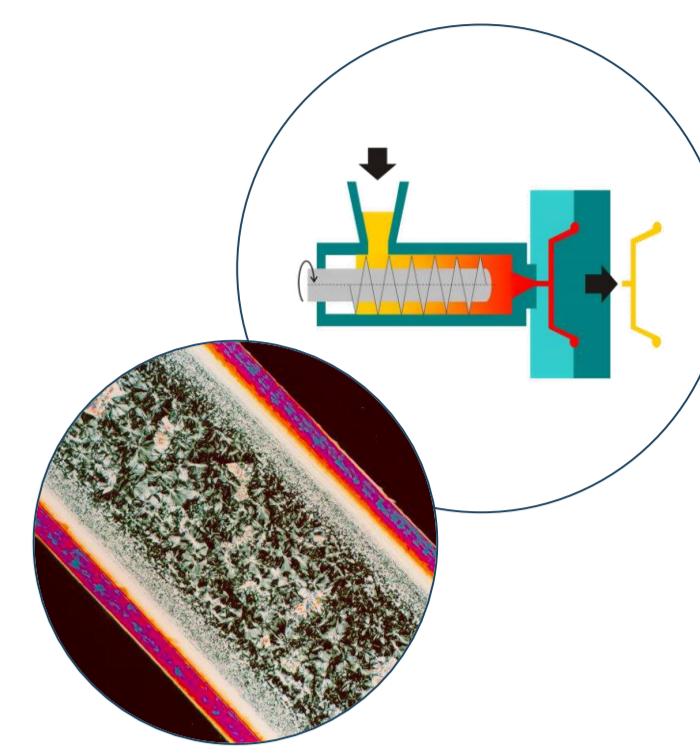
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Step-like pressure changes during polymer solidification are often encountered in melt processing (e.g. injection moulding). Similar to the effect of shear flow pulses, short-term pressurizations can **accelerate crystallization** process due to the formation of **additional nucleation precursors**.

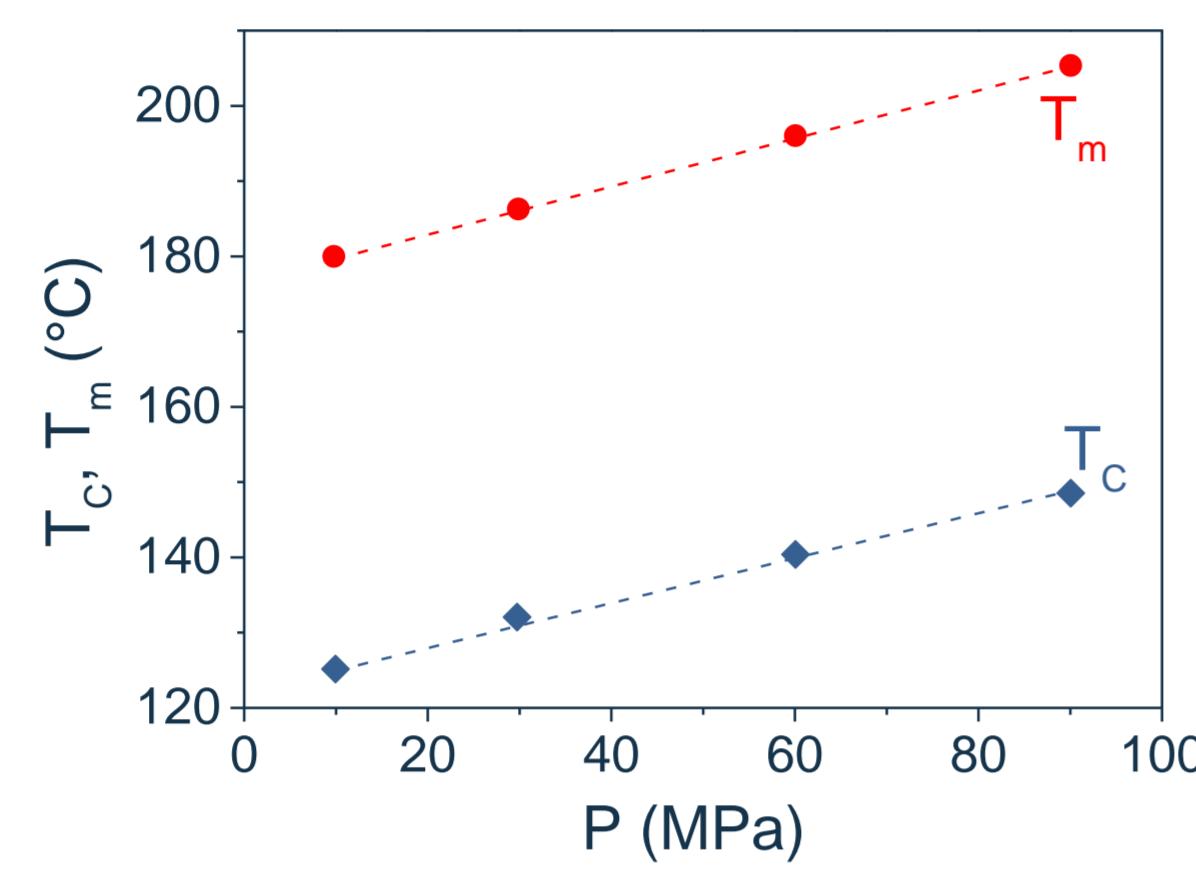
We investigate effect of **hydrostatic pressure pulses** on the crystallization kinetics of isotactic polypropylene by means of high pressure dilatometry and in-situ X-ray diffraction to assess **specific volume/crystallinity changes during isothermal crystallization** upon pressure pulses.



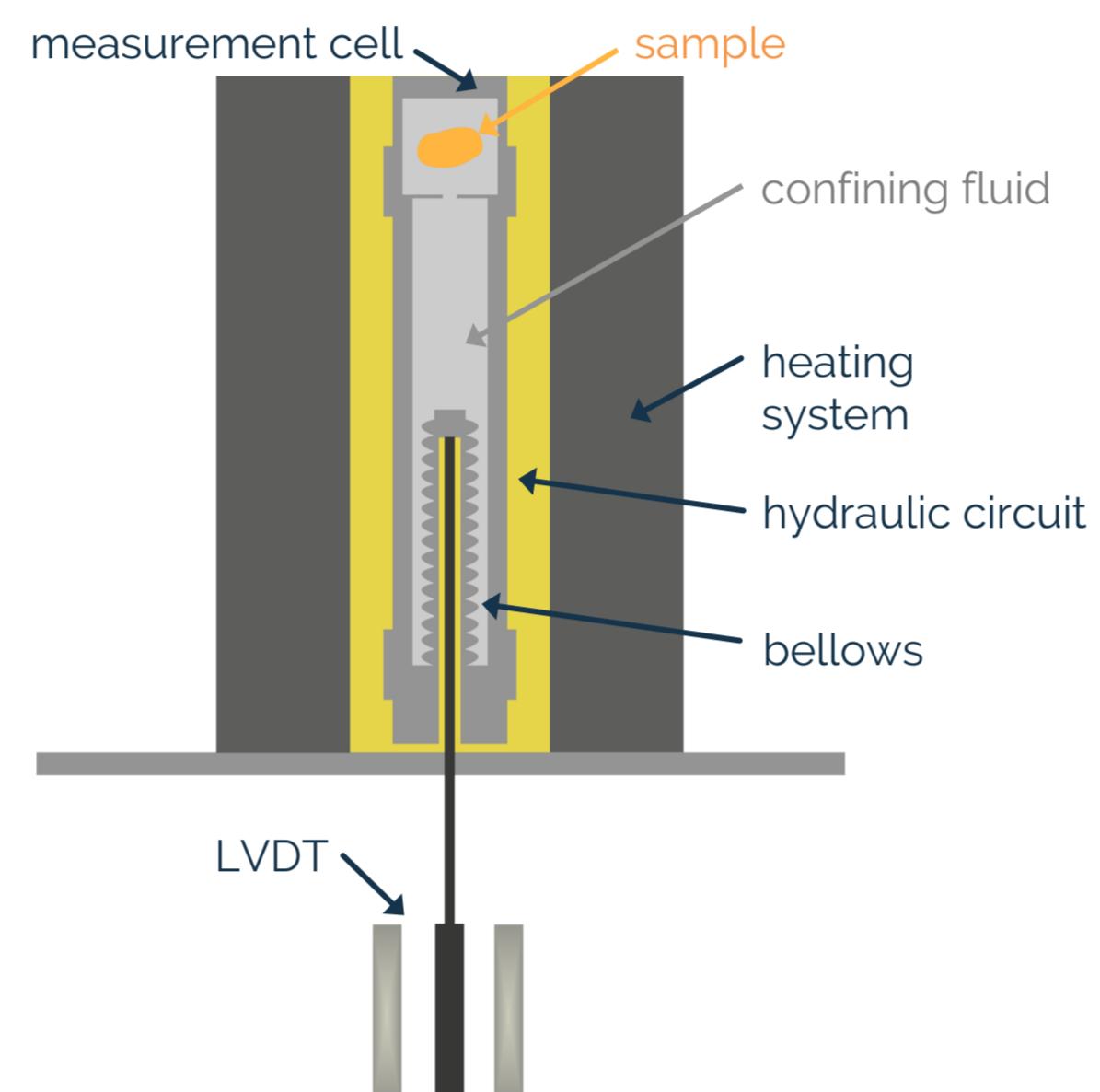
Experimental

Material

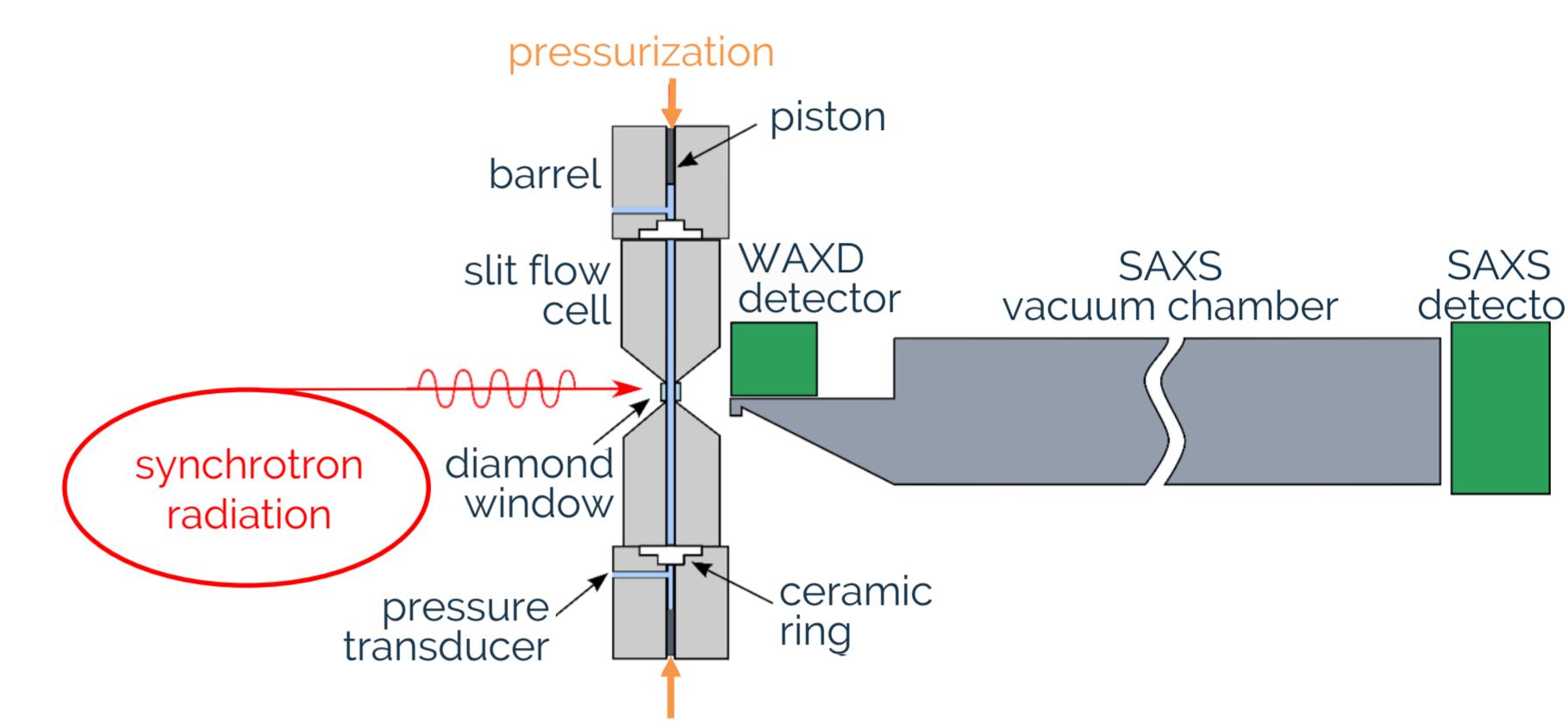
i-PP pellets
Mw = 365 kg/mol
Mw/Mn = 5.4
Tg ≈ -10 °C



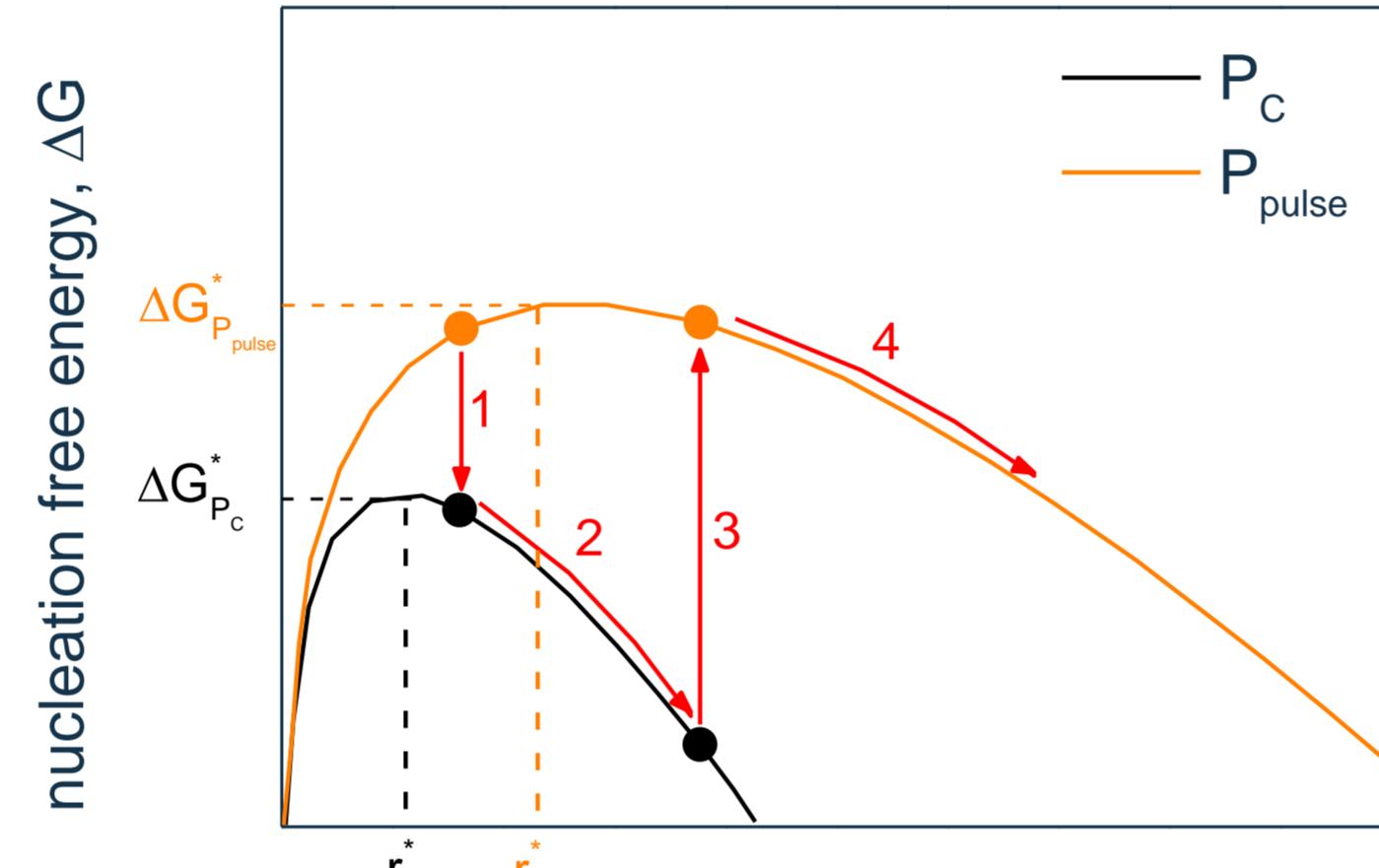
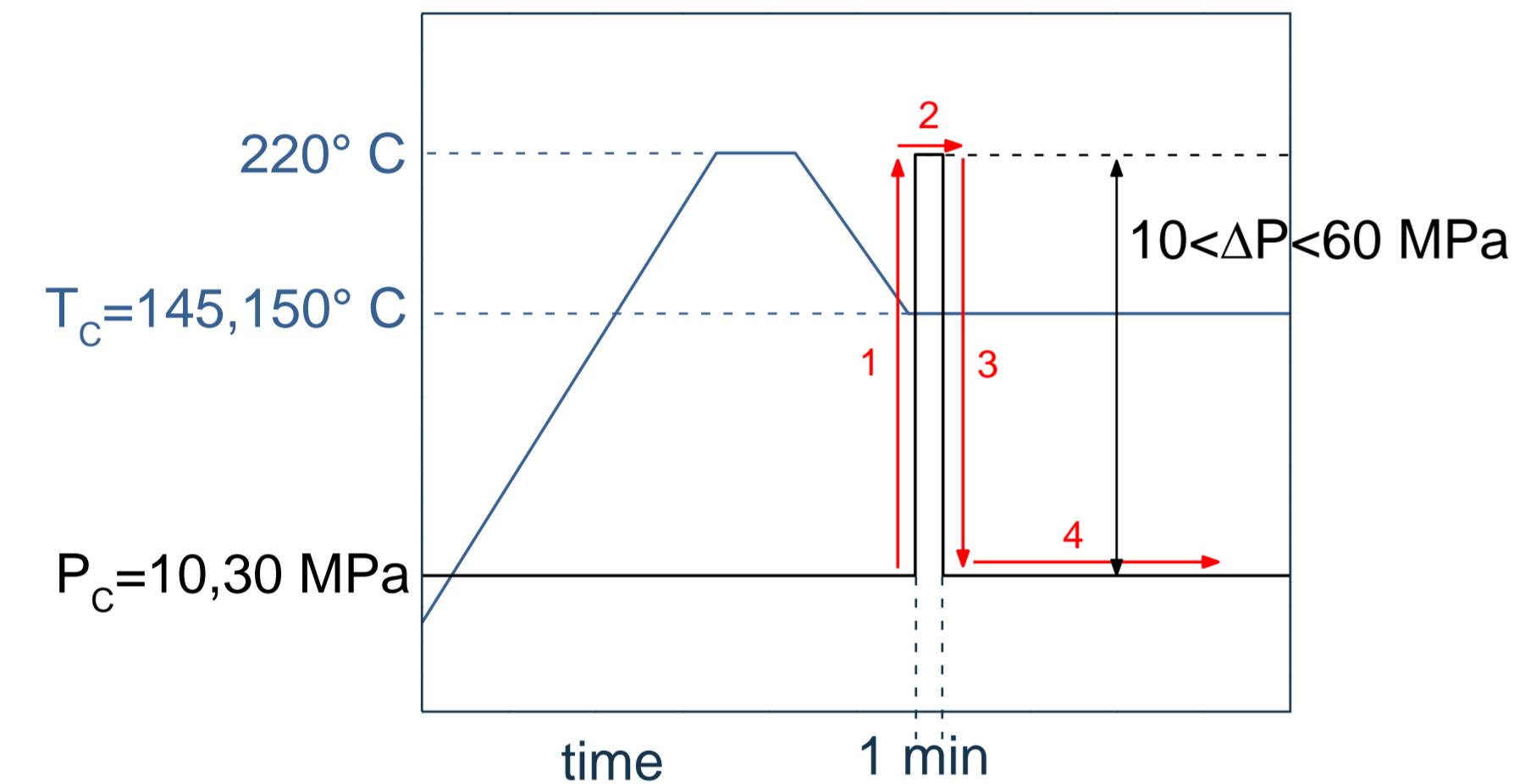
Confining fluid dilatometry



In-situ X-ray diffraction



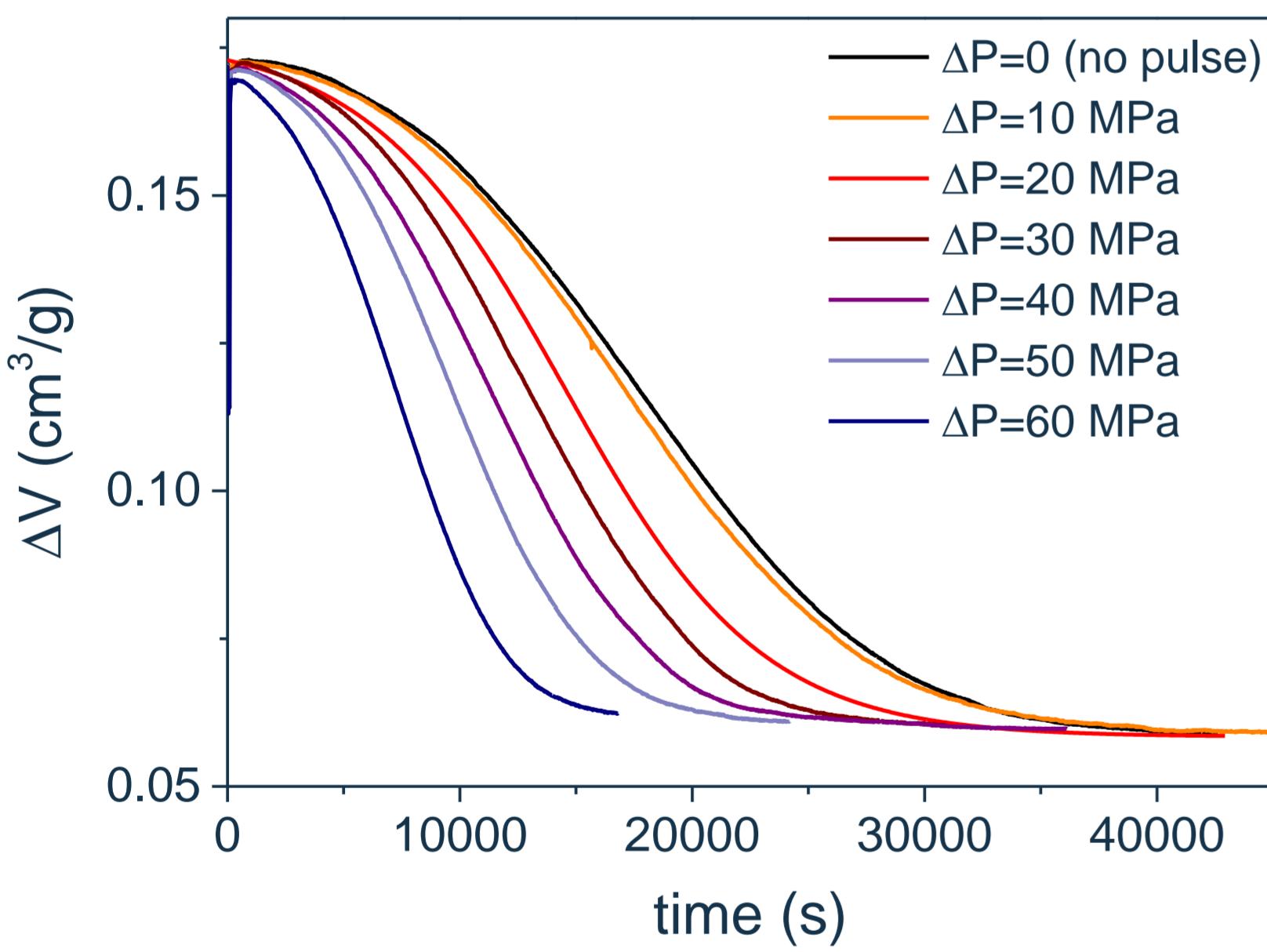
'short-term' pressure protocol



t pressurization << t crystallization

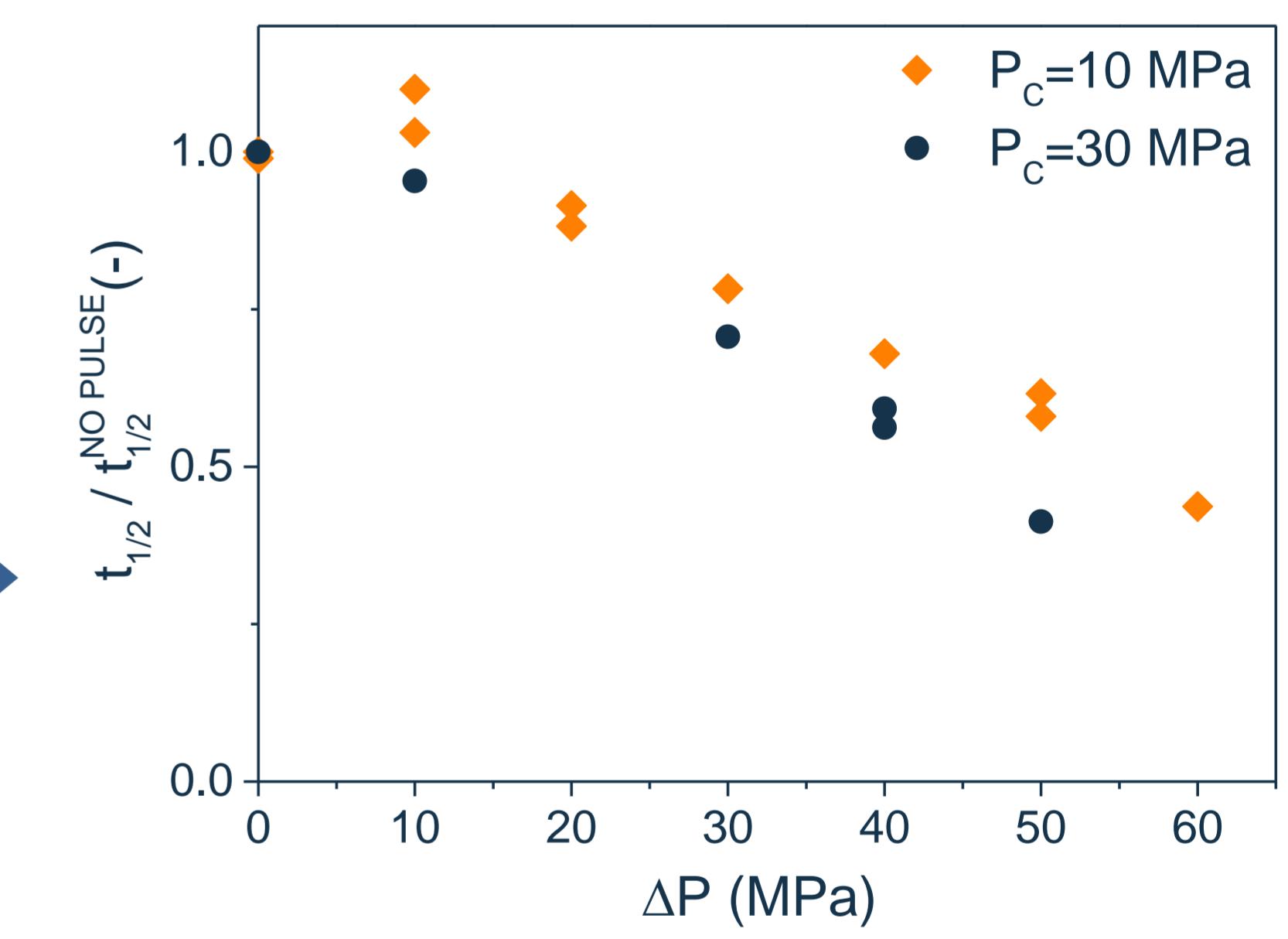
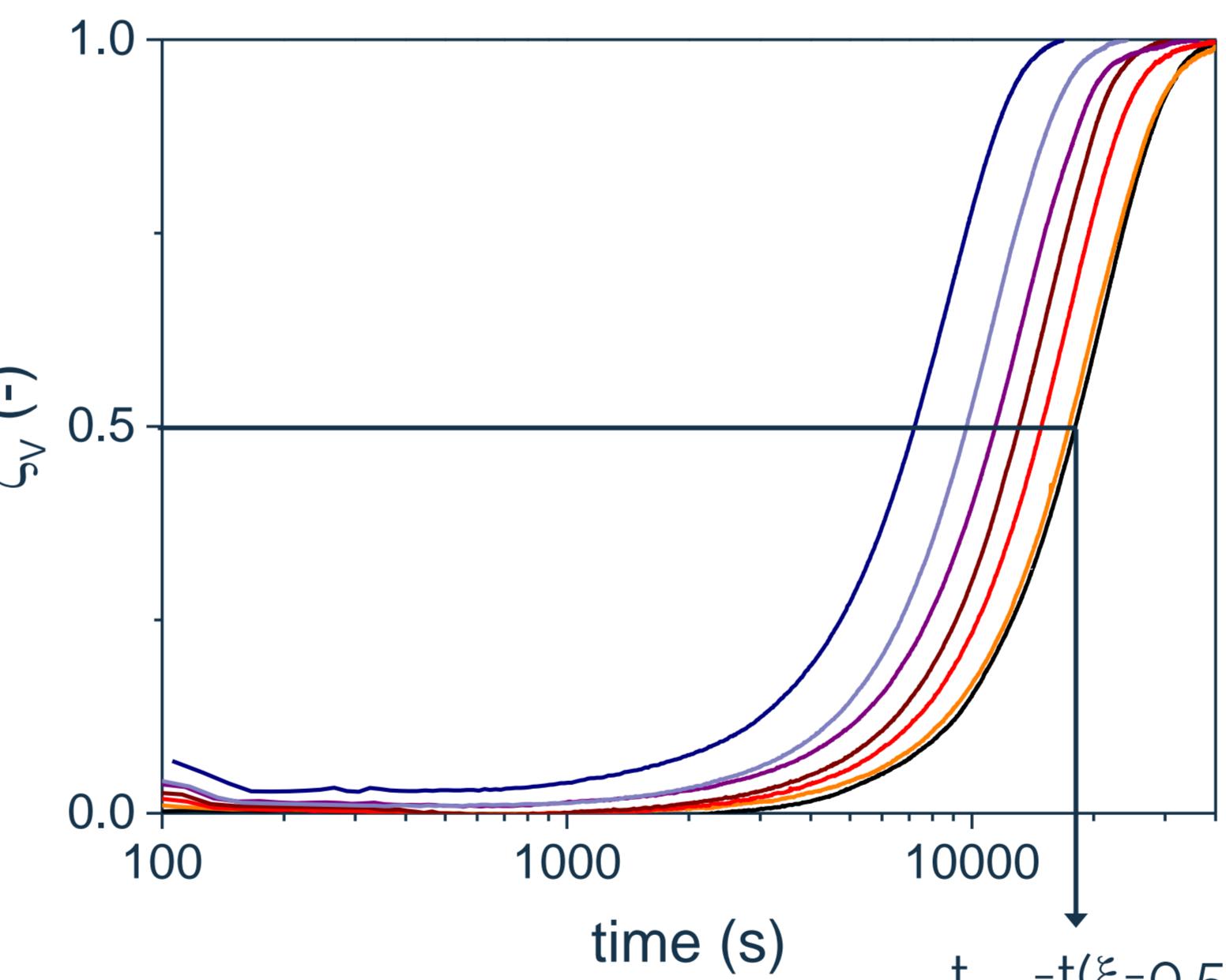
nucleation separated from spherulite growth

Results



space filling

$$\xi(t) = \frac{\tilde{V}_0 - \tilde{V}(t)}{\tilde{V}_0 - \tilde{V}_\infty}$$



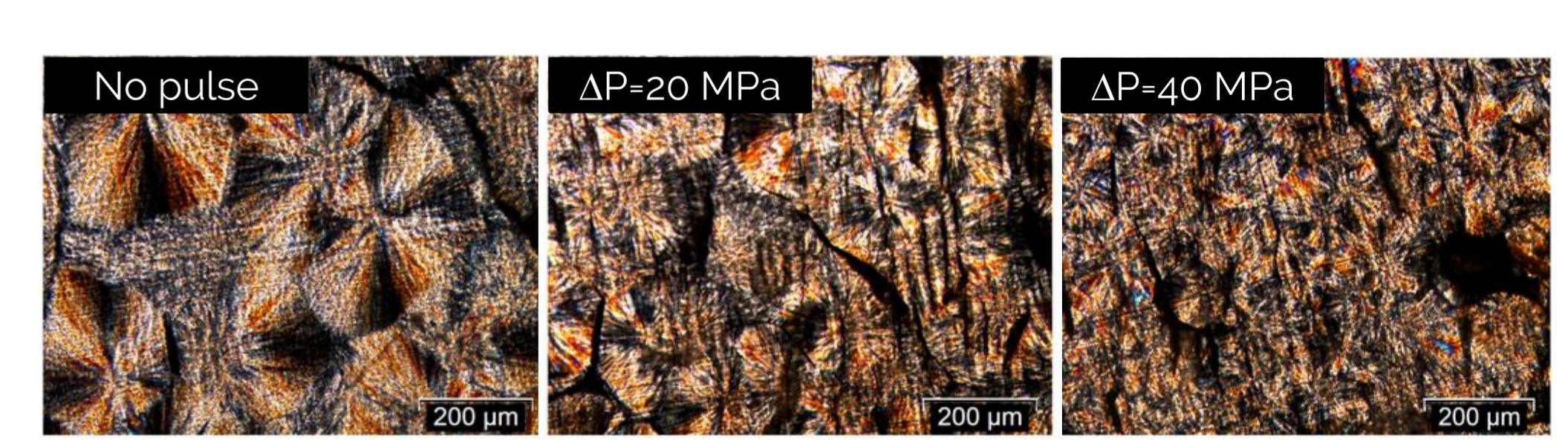
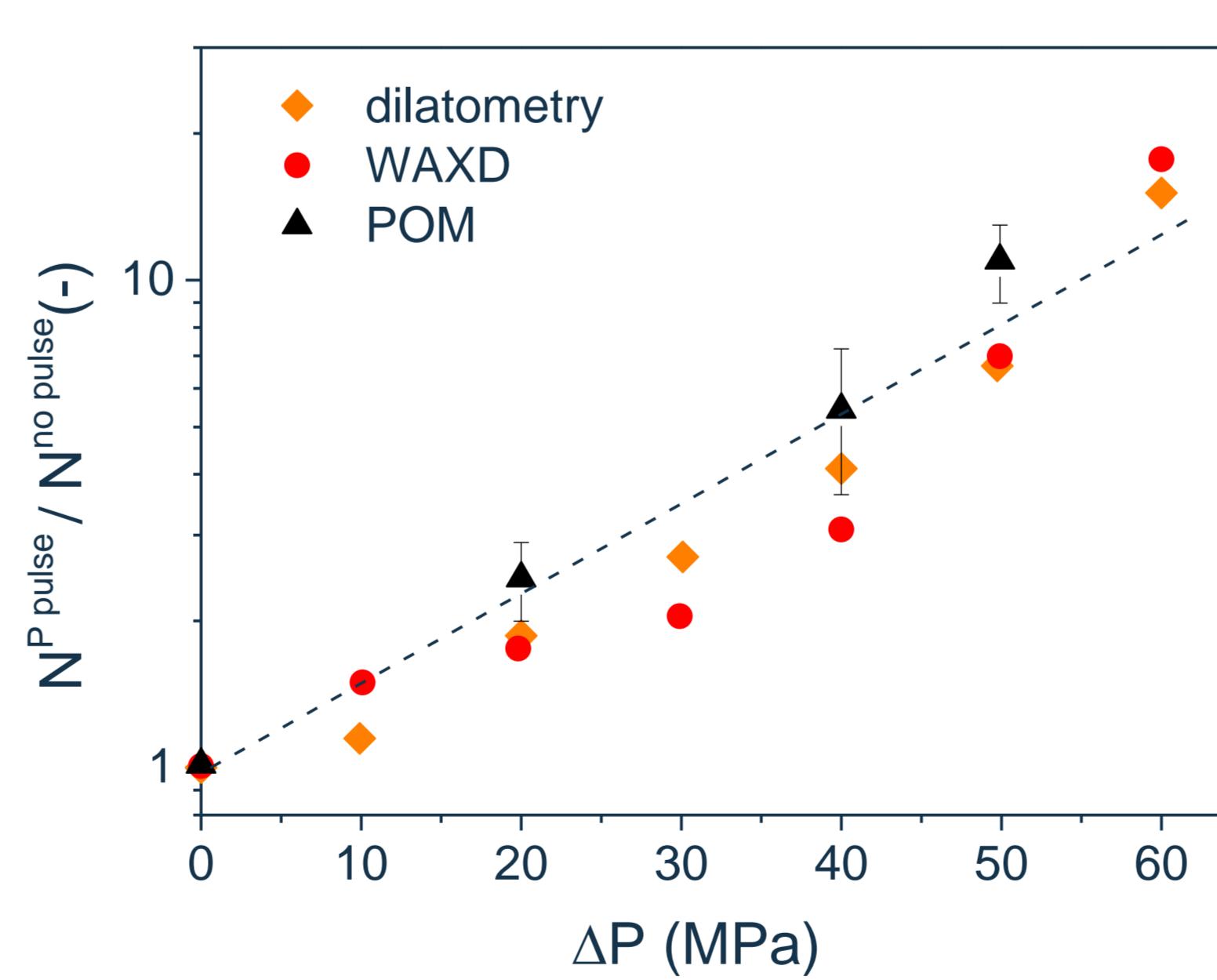
Avrami theory

Assuming three-dimensional heterogeneous nucleation:

$$\xi(t_{1/2}) = 1 - \exp(KNG^3 t^n) = 0.5$$

$$\frac{N^{P_{\text{pulse}}}}{N^{N_{\text{no pulse}}}} = \left[\frac{t_{1/2}^{N_{\text{no pulse}}}}{t_{1/2}^{P_{\text{pulse}}}} \right]^n$$

relative nucleation density



ΔP increases

number of active nuclei increases

Conclusions

- Enhancement of crystallization kinetics proportional to magnitude of pressure pulse
- Pulse magnitude have no effect on final amount of crystallinity
- Acceleration is linked to increase of number of active nuclei after the short term pressurization, as confirmed by ex-situ optical microscopy observations

References

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P. Zoller, Y.A. Fakhreddine, Thermochimica Acta, 238 (1994) 397-415

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