

SL 8.4

## The Influence of Cooling Rate and Melt Shearing on the Specific Volume of Polymers at Elevated Pressures

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A dilatometer was designed and built to study the influence of processing conditions on the (bulk) specific volume of semi-crystalline polymers and their related crystalline morphology. Experiments were done on two grades of isotactic polypropylene. Investigated processing parameters are pressure (20 – 60 Mpa), temperature (up to 210 °C), average cooling rate during crystallization (0.1 – 35 °C/s), and shear rate (up to 77 1/s). In general, the temperature marking the start of crystallization ( $T_c$ ) shifts towards lower temperatures with increasing cooling rate, the transition resulting from crystallization is less abrupt while the specific volume after complete cooling increases. As an example, for the lowest and highest cooling rate applied at a pressure of 40 Mpa a shift in  $T_c$  of 30 °C is observed while the specific volume after complete cooling increases with about 1.4%. The influence of shear flow is investigated by applying a step shear during cooling, i.e. non-isothermal conditions. Two shear rates are applied (38.5 and 77 1/s) while the total shear is kept constant at 117. Shear is applied at temperatures either well above the experimental melting point  $T_m$ , at medium supercooling, or at large supercooling. In general, shear shows a significant influence on  $T_c$ , shifting it towards higher temperatures indicating enhanced crystallization kinetics. Wide angle X-ray scattering (WAXS) experiments performed *ex situ* show that this shift can be positively linked to orientation of the crystalline morphology. Depending on the material's molecular weight distribution and pressure level, even shear flow applied at a temperature well above  $T_m$  has a significant effect on specific volume and the resulting morphology. With increasing pressure, shear rate, molar mass ( $M_w$ ) or decreasing temperature where shear flow is applied the crystallization process is enhanced resulting in a stronger oriented crystalline morphology.