Polymorphism and crystal transition are of great significance for property mediation in polymer materials. Isotactic polypropylene (iPP) with β-crystal has been widely utilized for the preparation of high performance plastics or films. In the present work, the structural evolution of initially isotropic β-nucleated iPP (β-iPP) during uniaxial stretching at different temperature was investigated by in-situ X-ray scattering using synchrotron radiation. The wide-angle X-ray scattering (WAXS) results confirmed that the β-crystal transformed either to the mesophase at lower temperature (30 °C) or to the α-crystal at higher temperature (60, 100 and 120 °C) during stretching. Unusual orientation of β-crystal with molecular chains perpendicular to the tensile direction was identified. As revealed by small-angle X-ray scattering (SAXS), cavitation took place in β-iPP stretched at temperature lower than 120 °C. The size and shape of the cavities were observed by scanning electron microscopy. The deformation mechanism of β-iPP combining the crystal transition, cavitation and orientation was proposed.