Influence of thermal history on phase behavior and morphology of PP

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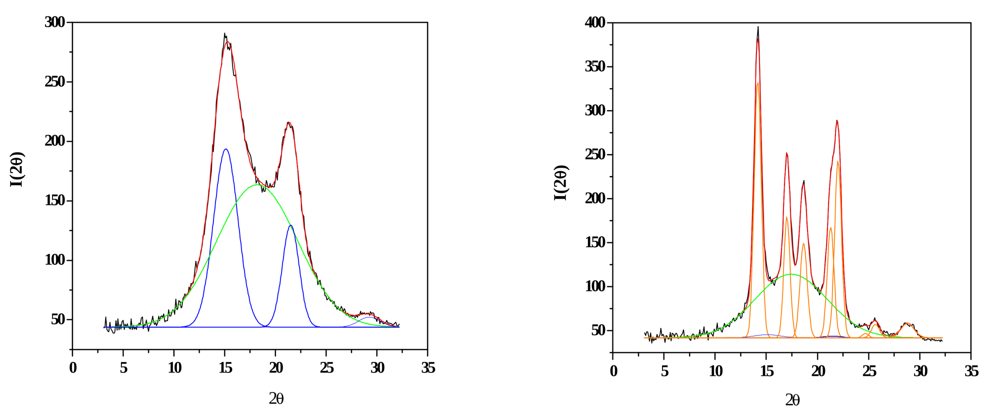
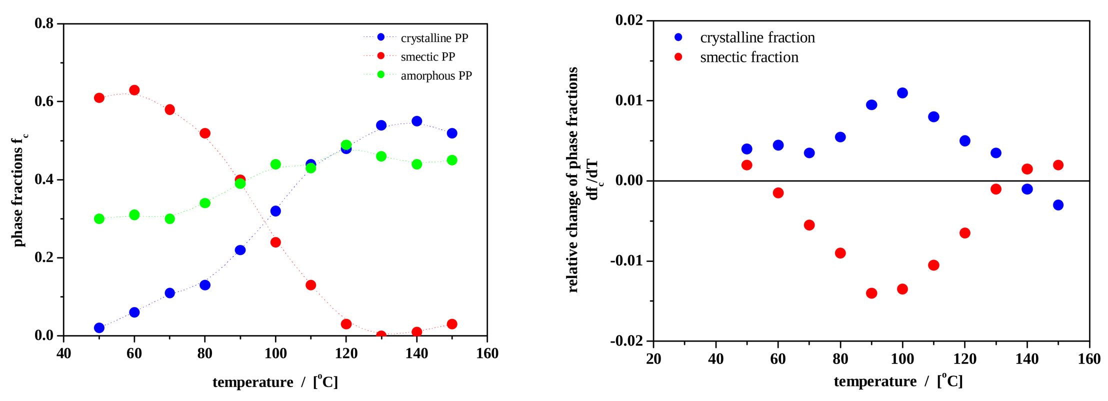
1. Introduction

In a previous report [1] structural aspects of polypropylene have been studied via X-ray diffraction employing different thermal histories. Whereas upon slow cooling crystallization of polypropylenes progresses into the monoclinic α-phase, ultra-fast cooling (via quenching between cold metal plates) below the glass temperature of PP can entirely suppress crystallization. However, in contrast to fully amorphous materials, the non-crystalline phase of polypropylene reveals (short-range) order among the helical segments, the so-called mesomorphic phase.



X-ray diffraction pattern: PP homopolymer after quenching from 200°C between cold metal plates (left) and after cooling with 10°/min (right); the results from deconvolution into contributions from mesomorphic (blue), crystalline (orange) and amorphous phase (green) is indicated

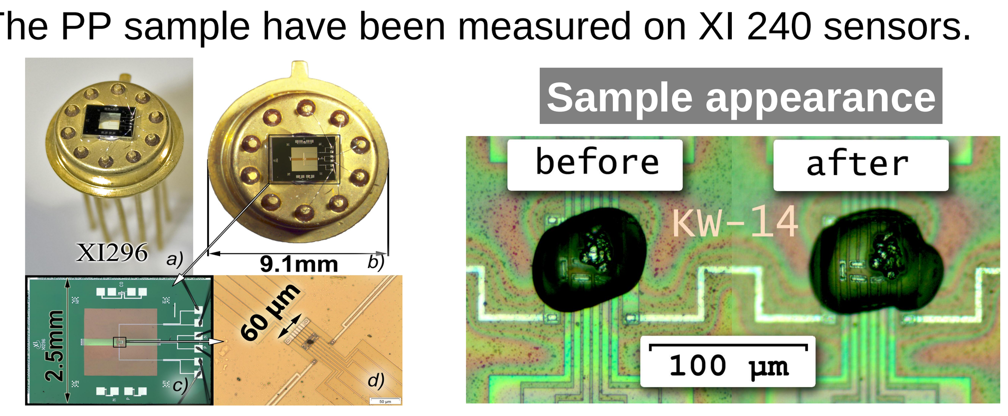
Combining the results from temperature dependent X-ray diffraction experiments with Fast Scanning Calorimetric studies yielded unique insight into the structural and morphological changes of these systems during the cold crystallization process. An interesting finding that emerged from the XRD studies concerned the stability of the mesomorphic phase. From the perspective of XRD, even extended annealing of the mesomorphic material under ambient conditions did not significantly alter the morphology, i.e. arrangement of the helical sequences with respect to each other whereas DSC experiments suggested some changes in the thermograms after extended annealing periods.



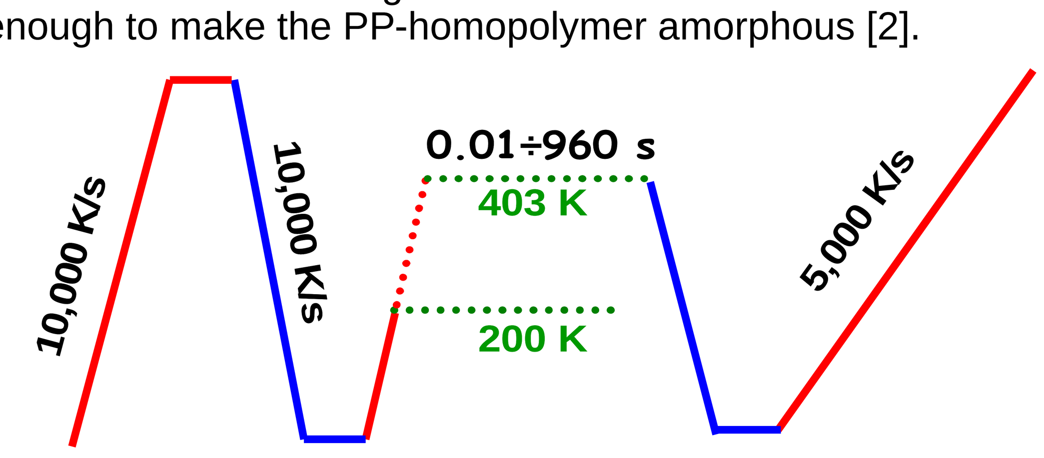
Relative amounts of amorphous, crystalline and mesomorphic phase, obtained via deconvolution of temperature dependent XRD data recorded from PP homopolymer; r = 2°/min, exposure time 30s (left) and relative changes in the phase composition at different temperatures (right)

2. Quench and annealing experiments (UFDSCC)

The PP sample have been measured on XI 240 sensors.

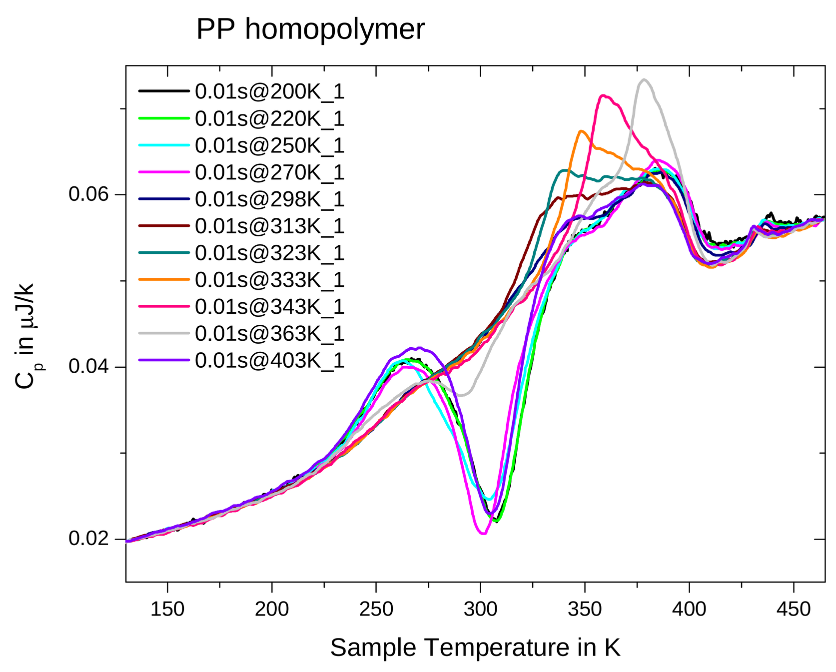


Time-temperature profile of the treated PP-homopolymer sample. The PP homopolymer has been heated until the melt (T~200 ° C) and subsequently quenched at a cooling rate of 10 000 K/s. This cooling rate has been defined to be fast enough to make the PP-homopolymer amorphous [2].

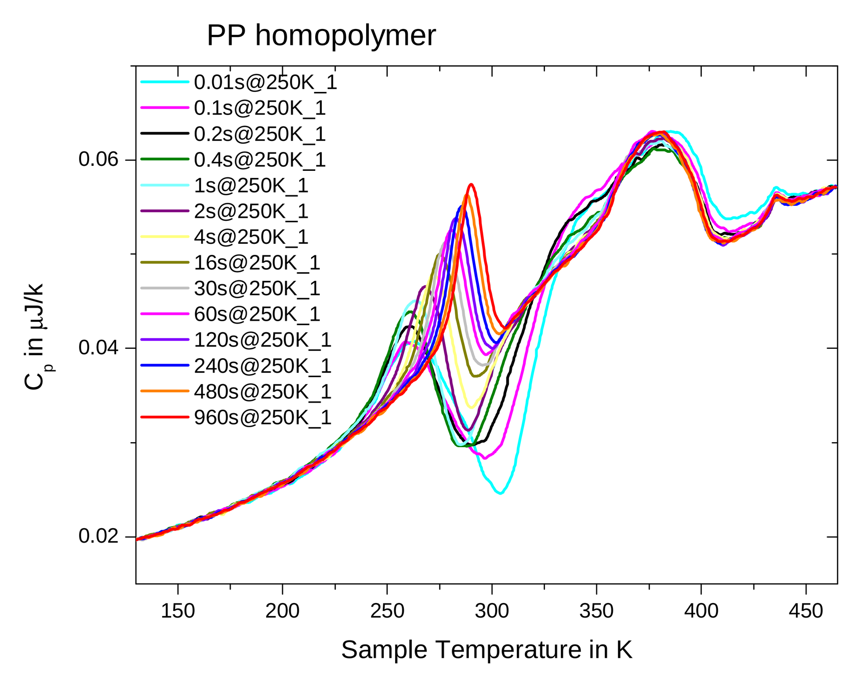


3. UFDSCC heating curves

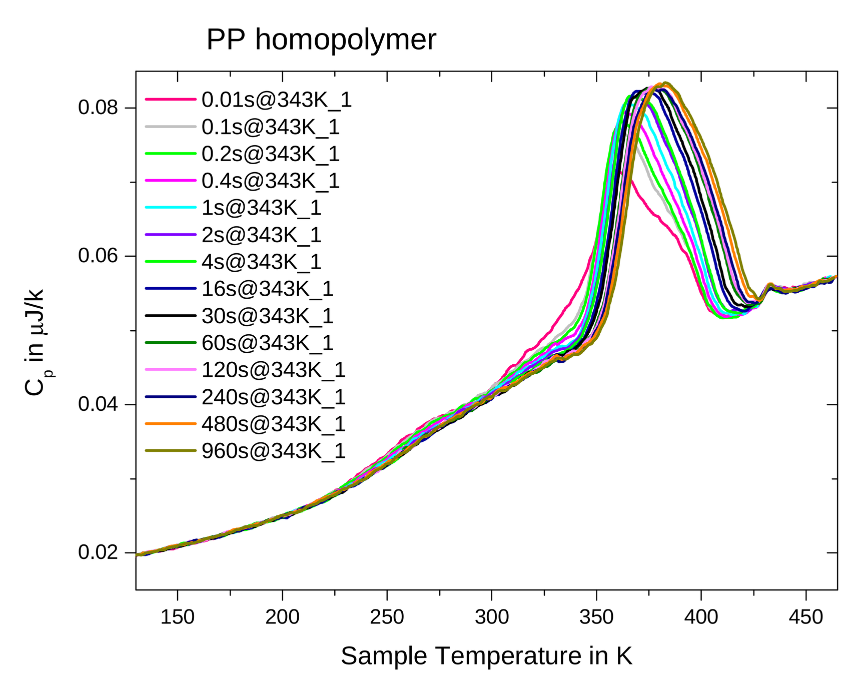
Starting from temperatures below the glass transition temperature (Tg ~ 250 K) the subsequent heating curves clearly show the Tg immediately followed by a cold crystallization (= crystallization during heating) and a direct melting of these cold crystallized material (Tiso from 200 up to 270 K). At 298 K, far enough above Tg, the cold crystallization is disappeared which means reorganization/crystallization took place during the very short annealing period (0.01s) at this temperature. The fast reorganization/crystallization settles immediately in for annealing temperatures up to 343K. It is remarkable that, for the annealing temperature of 363 K suddenly cold crystallization appears again but only to a low extent while at an annealing temperature of 403 K cold crystallization is back to its full extent.



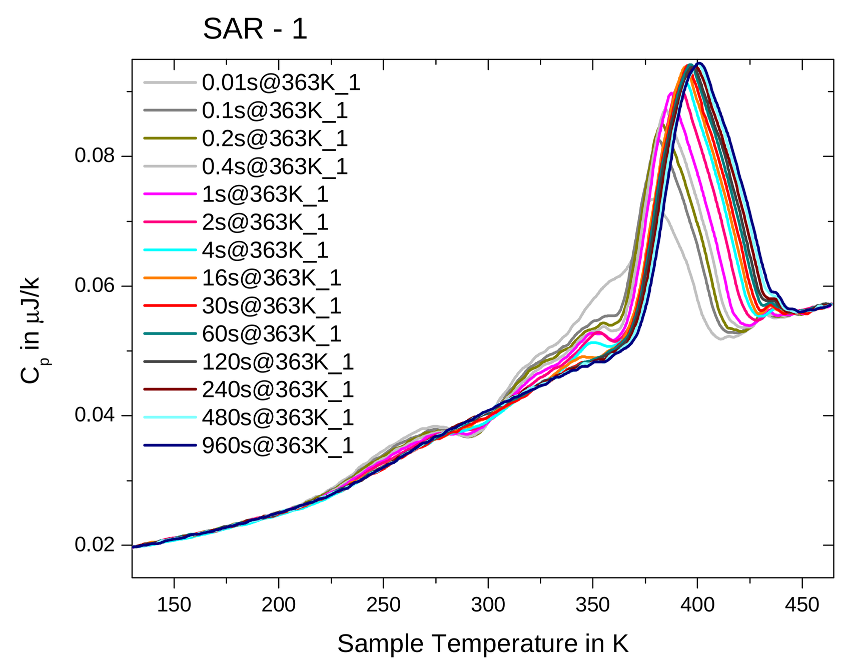
The cold crystallization area is present to a full extent at the shortest annealing time. With the increase of time this area decreases which means that the material has got more time to reorganize into a more ordered state during annealing. The subsequent melting peak area in the range of approximately 350-400 K remains unchanged with respect to the annealing time. This peak stands for the melting of the phase organized during cold crystallization and annealing cumulatively.



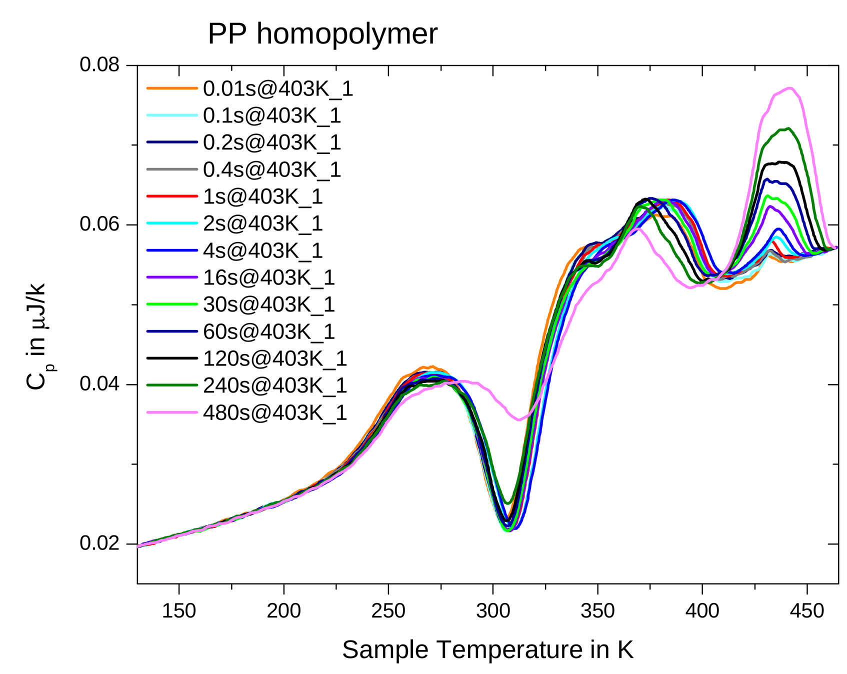
The UFDSCC curves for various annealing times at well defined temperatures as 298K, 313K, 323K, 333K and 343K reveal no cold crystallization but double peak melting behavior reflecting both annealing temperature (left) and the melting after reorganization. The absence of cold crystallization starting from the shortest annealing time at the mentioned temperatures can be explained by the increase in mobility with increase of the temperature gradient with respect to Tg.



It is remarkable to mention that the cold crystallization area is rather small compared to the full extent of the previously observed ones. Moreover it disappears at 4 sec annealing time. But the cold crystallization at this annealing temperature cannot e linked towards smectic phase formation due to very high mobility (far above glass transition temperature) but rather towards the higher order/perfection crystal formation.



On contrary to the results of 363K annealing temperature the cold crystallization appears to the highest extent after keeping the sample even for 0.01 sec at 403K. This maximum of cold crystallization area remains constant up to such long annealing time of 120 sec which means that the kinetics of the cold crystallization behavior is much slower than that of smectic phase formation at temperatures of 298K up to 343K.



4. Conclusions

- Structural studies on quenched polypropylene can presently only be performed under ambient conditions; in this case XRD reveals the mesomorphic form with short range order among helical segments
- Our observations suggested that the relative amounts of mesomorphic and amorphous form in quenched polypropylene may vary significantly in the quenched materials; phase composition, however, is essentially maintained from the viewpoint of XRD even after prolonged storage times
- Annealing at different temperatures under controlled conditions by UFDSCC results in the several different thermal behaviors on subsequent heating curves which speaks about the formation of various morphology of the samples

5. References

[1] Ralf Kleppinger, Internal DSM Report 2008-03-00501

[2] D. Mileva, R. Androsch, E. Zhuravlev, C. Schick Thermochimica Acta 492 (2009) 67-72.