

Review of the doctoral thesis entitled as

Controlling Innovative Polyolefin Properties by Structural Transformations

written by

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In this work, isotactic polypropylene and isotactic poly(1-butene) are investigated by using wide range of experimental techniques/devices such as wide-angle X ray scattering, differential scanning calorimetry, scanning electron microscope, gel permeation chromatography, tensile testing, X-ray photoelectron spectroscopy, atomic force microscopy, contact angle measurement, oscillatory rheometry, Fourier transform – infrared spectroscopy in order to determine interrelations between structure, processing and their macroscopic properties with specific attention to the following subjects:

Isotactic polypropylene

- Effect of thermal history and molecular weight on the specific β -nucleation.

Isotactic poly(1-butene)

- Effect of annealing temperature on phase composition and tensile properties.
- Effect of plasma treatment on surface structure and properties.
- Effect of photodegradation on degradation kinetics, crystallization, thermal properties and phase transformation.

The following research findings can be considered as the most important:

- The isotactic polypropylene molecular weight increase leads to decrease in β -nucleation activity.
- Annealing temperature affects the overall rate of polymorphic changes in isotactic poly(1-butene) but the resulting mechanical properties (tensile modulus, elongation and strength at break) are controlled solely by the extent of this transformation.

- The gradual changes in surface hydrophilicity/hydrophobicity of plasma-treated isotactic poly(1-butene) samples can be attributed to the variation of the conformation of plasma-introduced functional groups.
- Photodegradation, which was found to be faster in isotactic poly(1-butene) with lower-molecular weight, retards the phase transformation.

The obtained Ph.D. thesis results have already been published (Paper 1, *Macromolecules*, IF(2010)=4.838; Paper 2, *Journal of Applied Polymer Science*, IF(2010)=1.240; Paper 4, *Polymer Degradation and Stability*, IF(2010)=2.594) or have been submitted to publication (Paper 3). Obtained results represent significant contribution to the current knowledge and understanding of isotactic polypropylene and isotactic poly(1-butene) behavior and some of them have direct practical importance for application in industry.

Comments and questions:

1. Description of each individual atom is missing in Figures 1.1, 1.3 and 2.1.
2. Page 14, lines 2-5: The statement that isotactic poly(1-butene) is, from commercial point of view, more important than metallocene syndiotactic poly(1-butene) should be explained here in more detail.
3. Page 19, line 18: ‘... oxygen diffusin ...’ should be written as ‘... oxygen diffusion ...’
4. Page 30, line 2: What justify to use the term ‘novel polyolefins’ in this place?
5. Page I:4, Can the results presented in Figure 12 be also explained by the flow induced crystallization taking place during the applied compression molding? Was the closing rate, dh/dt (or the force F required to fill out the mold) the same in all cases so the applied flow field is comparable for all tested samples? Note that for Newtonian fluid the F can be defined as follows:

$$F \approx C \eta_0 \frac{dh}{dt}$$

where C is the geometrical constant, η_0 is the Newtonian viscosity, h is the sample thickness, t is the time. In the light of this point, (i.e. if the specific care is not paid to application of constant dh/dt or F during the compression molding of polypropylene samples having significantly different Mw) one could expect that samples with lower Mw, η_0 are much easier to mould (dh/dt is high) in contrary to samples having higher Mw, η_0 (dh/dt is low), which could cause different flow history (depending on Mw) which could affect the further sample analysis.

6. Page II:3 Is it possible to apply the Time Temperature Superposition (TTS) principle for data described in Figure 2? If yes, could the author comments the possible benefits of such procedure with respect to isotactic poly(1-butene) phase transformation phenomenon?

7. Page III:14 In the Figure 1 caption, the statement that the full circle symbol represents Contact Angle (CA) of untreated isotactic poly(1-butene) sheets is missing. What might be the reason for CA decrease in the case of homoPB treated by Ar and Ar/C₃H₅NH₂ plasma within 0-300 minutes time interval?
8. Page III:9, Page III:17, Figure 4, Page III:18, Figure 5: Why the symmetrical Gauss-Lorentz functions are preferably chosen to fit the data depicted in Figures 4-5?
9. Page IV:2, second column, line 6: Why the 8mm diameter instead of standard 25mm diameter parallel plate geometry was utilized during rheological characterization of isotactic poly(1-butene)? What was the applied shear strain during the performed rheological measurements?
10. Page IV:2, second column, line 13, Eq. 2, line17: the η symbol is missing.
11. Page IV:2-3, 3.1. Rheological behavior chapter: More detailed information about molecular changes in the isotactic poly(1-butene) during photodegradation could be extracted from the obtained rheological measurements by determination of relaxation spectra, which unfortunately, has not been done in this work.

Conclusion:

The Ph.D. student Lenka Chvátalová has proved a high ability to do independent research in the area of polymer science. She was able to handle variety of experimental techniques for the characterization of polymers, and by using the obtained results to make right conclusions with respect to defined research aims. The results summarized in her Ph.D. thesis are significant and considerably extends the current knowledge about understanding interrelations between structure, macroscopic properties and processing of isotactic polypropylene and isotactic poly(1-butene). Thus **I fully recommend this Ph.D. thesis for final doctoral defense**.

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