

Zabrze, April 9, 2015

**COMMENTS ON THE PHD THESIS ELABORATED BY MAŁGORZATA WOJTCZAK-MICHALSKA**  
**FROM THE CENTRE OF MOLECULAR AND MACROMOLECULAR STUDIES, POLISH ACADEMY OF SCIENCES,**  
**ON “THE INFLUENCE OF CHEMICAL COMPOSITION AND NUCLEATION ON ALIPHATIC-AROMATIC**  
**COPOLYESTERS’ CRYSTALLIZATION”,**  
**UNDER THE SUPERVISION OF PROFESSOR ANDRZEJ GAŁĘSKI**

The PhD thesis of Małgorzata Wojtczak-Michalska is devoted to the crystallization behaviour of selected aliphatic-aromatic copolyesters with various chemical compositions. The thesis has been completed at the research group of Professor Andrzej Gałęski. Therefore, it is not surprising that it was oriented on the subject of research excellence of the supervisor.

The alignment of the thesis is rather “classical” and it comprises: abstract (both in English and Polish), introduction, state of knowledge (33 pages), objective of the thesis, experimental part, results and discussion (65 pages) as well as the Appendix where the results of the selected aliphatic-aromatic copolyester biodegradability (conducted at the Institute of Biopolymers and Chemical Fibres) have been briefly presented. Thus, the appropriate balance was achieved between the literature survey and the discussion of the presented results. Moreover, Małgorzata Wojtczak-Michalska attached at the end of the dissertation the list of publications, patents and presentations where she was co-author.

The literature survey related to the subject of the thesis is well written and includes the most important aspects of the (co)polymers crystallization. The minor remark concerns the chapter 1.1 (Polyesters) where the author did not mention ring-opening polymerization as a synthetic way to biodegradable polyesters. Analysis of the state of knowledge led the author to the conclusion, that in the literature there are no reports on synthesis of a random copolyesters containing altogether the adipate, succinate, glutarate and terephthalate units.

Therefore, for the purpose of the thesis PBASGT copolyesters: poly(butylene adipate-co-succinate-co-glutarate-co-terephthalate) varying in the ratio of aromatic component (from 10 up to 90%) have been synthesized. Moreover, the influence of chemical composition on nucleation of crystallization and on crystallization of aliphatic-aromatic copolyesters (AAC), has not been deeply previously studied.

One of the main goal of the dissertation was to specify the optimal chemical composition of AAC, that would combine susceptibility to biodegradation and good physical performance. AAC with different composition were synthesized at the Institute of Biopolymers and Man-Made Fibers, Łódź, Poland. The  $^1\text{H}$  NMR spectroscopy has been used for assignment of proton resonance of homogeneous and heterogeneous dyads, the average block length and the degree of randomness over the range of AAC composition studied. Several techniques have been used for characterization of AAC, and namely differential scanning calorimetry (DSC), wide- and small-angle X-ray scattering (WAXS, SAXS), size exclusion chromatography (SEC), atomic force microscopy (AFM), polarized light microscopy with hot stage (PLM) and light depolarization technique (PLD). Moreover, the chemical structure, morphology and crystallization behavior of PBASGT were compared with commercial aliphatic-aromatic copolyester of butylene terephthalate and butylene adipate (PBAT), Ecoflex®.

Results and discussions are presented in a very logical way and were devoted to the studies on influence of chemical structure and composition on copolyesters properties, crystallization characterization of selected copolyester and on nucleation of copolyester. The main goals of the thesis have been achieved. The author estimated the distribution of comonomer units along macromolecular chains of PBASGTs and correlate sequence distribution with their crystallization ability. The behavior of PBASGTs to form crystals such as nucleation of crystallization has been characterized. However, the undertaken selection of a composition of copolyester, which balanced processability, good mechanical and thermal properties with susceptibility to biodegradation may be a subject of dispute. The biodegradation studies of the selected PBASGT polymer during the incubation in compost were performed at the Institute of Biopolymers and Chemical Fibres, and results are included as Appendix to the dissertation. The PBASGT contained 45% of aromatic component was selected for the studies. The dependence of the weight loss of PBASGT polymer on the biodegradation time in the compost at 58°C was evaluated (Figure 5.57) and photographs of PBASGT film after specified time of degradation in the compost were presented (Figure 5.58). Such macroscopic observations were not supported by the molar mass changes evaluation and what is more important by the NMR studies on the

eventual changes of the copolymer composition during the biodegradation. Previous studies on Ecoflex® degradation in soil and on its ecotoxicological impact revealed the retention of aromatic chain fragments in the low molar mass fraction of the incubated sample (compare e.g.: *Biomacromolecules* 2010, 11, 839–847). Thus, more detailed biodegradation experiments on the novel PBASGT would be advisable in the future. Nevertheless, the thesis contains many interesting and original results. Both classic polymer and new, original systems have been considered and studied. The author managed to use polymer physics in the characterization of novel copolymers, establishing structure-properties relations – using advanced instrumental techniques. Most of the patented results are of real interest for different specific applications. The originality of the results is also proven by their publication in international journals or by their presentation at national/international conferences.

In my opinion, the dissertation truly reflected the influence of chemical composition and nucleation on aliphatic-aromatic copolyesters crystallization. Thus, I consider that Małgorzata Wojtczak-Michalska deserves to receive the doctor degree and in my opinion the dissertation fulfills all requirements for Ph.D. Theses stated in the Polish law (the Act on Scientific Degrees and Title). Consequently, my recommendation to the Scientific Council of CMMS PAS is to proceed into the next steps of PhD qualification procedure of Małgorzata Wojtczak-Michalska.

Moreover, taking into account the scientific value of the results presented in dissertation, verified by the international scientific community, I recommend to distinguish the Ph.D. Dissertation of Małgorzata Wojtczak-Michalska.

  
Marek Kowalczyk