

THE INFLUENCE OF CHEMICAL COMPOSITION AND NUCLEATION ON ALIPHATIC-AROMATIC COPOLYESTERS' CRYSTALLIZATION

Malgorzata Wojtczak^a, Andrzej Galeski^a, Slawomir Dutkiewicz^b, Ewa Piorkowska^a

^aCentre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, Lodz, andgal@cbmm.lodz.pl

^bInstitute of Biopolymers and Chemical Fibres, Sklodowskie-Curie 19/27, Lodz, grupasyntez@ibwch.lodz.pl

ABSTRACT

Aromatic polyesters such possess better thermal and mechanical properties in comparison to aliphatic polyesters. Therefore the incorporation of aromatic units along aliphatic polyester chains appeared to be a good concept to merge biodegradability characteristic for aliphatic polyesters and good thermal and mechanical properties typical for aromatic polyesters. However, aliphatic-aromatic copolyesters (AAC) are biodegradable under condition of sufficiently short sequences of aromatic units which was shown by Witt et al.¹. Moreover, Witt et al.² drew a conclusion that AAC remain biodegradable if the population of aromatic ester comonomers does not exceed 60 mol %.

Up to now, there have been reports about copolyesters possessing from one up to three aliphatic units and one aromatic. However, none of them focused on the influence of chemical composition and nucleation on crystallization of AAC, especially that too short sequences of crystallizable units may suppress crystallizability.

The aim of our studies, was to produce AAC, which would combine ability to biodegradation and good physical performance. Therefore, several copolyesters of poly(butylene adipate-co-succinate-co-glutarate-co-terephthalate) (PBASGT) differing in composition have been synthesized and characterized by ¹HNMR spectroscopy, wide- and small-angle X-ray scattering (WAXS, SAXS). Using the assignment of proton resonance due to homogeneous and heterogeneous dyads³⁻⁵, the average block length and the degree of randomness were investigated over the range of copolymer composition.

Most of the synthesized AAC were nearly random copolymers. Surprisingly, it appeared that they are able to crystallize. The increase of aromatic units contents caused an increase in crystallization temperature but did not change the crystallographic structure, in contrary to the results obtained by Li et. al⁶. In all the crystallizable copolyesters only butylene terephthalate (BT) blocks are able to crystallize in the crystallographic form characteristic of homo polymer. There are slight differences in several diffraction peak positions (not all) of synthesized copolyesters and aromatic homopolymer interpreted as stress-induced unit cell deformation.

A most promising composition with respect to biodegradability, thermal and mechanical properties was selected for further investigation of crystallization. The spectroscopy and X-ray methods were complemented by differential scanning calorimetry (DSC), polarizing light microscopy (PLM) and small angle light scattering (SALS). They revealed that PBASGT crystals form spherulitic aggregates filling the entire volume of the material with spherulites of average diameter around 7µm, which are formed from few nanometers thick fibrous crystals while the crystallinity reached 20%. The crystallization behavior of PBASGT is strongly driven by the presence of self-nucleation. Self-nuclei can survive the temperature up to 150°C. More extensive investigations led to the conclusion that the nucleating agents that are effective for PBT are also effective for PBASGT. Nucleation of PBASGT was very effective and shifted the nonisothermal crystallization peak from 70°C to 84°C during cooling at 10°C/min.

References

- ¹ Witt, U.; Müller, R. J.; Deckwer, W. D. *J. Environ. Polym. Degrad.*, **1996**, *4*, 9.
- ² Witt, U.; Yamamoto, M.; Seeliger, U.; Müller, R. J.; Warzelhan V. *Angew Chem Int Ed.*, **1999**, *38*, 1438
- ³ Kang, H. J.; Park, S. S. *J. Appl. Polym. Sci.*, **1999**, *72*, 593.
- ⁴ Park, S. S.; Kang, H. J. *Polym. J.*, **1999**, *31*, 238.
- ⁵ Shi, X. Q.; Aimi, K.; Ito, H.; Ando, S.; Kikutani, T. *Polym.*, **2005**, *46*, 751.
- ⁶ Li, F.; Xu, X.; Hao, Q.; Li, Q.; Yu, J.; Cao, A. *J. Polym. Sci.*, **2006**, *44*, 1635.