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Microstructure of Polymer Chains in Nanoparticles: NMR Spectroscopy and DFT Calculations

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Poly(alkyl- α -cyanoacrylate) (PACA) nanoparticles have been developed as colloidal drug carriers intended for an intralysosomal drug delivery by Couvreur et al. [1]. The possibility of lysosomal degradation is very important in relation to the biocompatibility of these polymers and could be a key to their successful functioning as drug delivery systems. The accessibility of the ester side bonds of poly(alkyl- α -cyanoacrylates) for the active site of hydrolytic enzymes should be closely related with the polymer chains microstructure and thereby could be a key factor for the rate of degradation and release characteristics of these polymers.

NMR spectroscopy and quantum chemical calculations were applied for structural characterization and determination of the preferred stereochemical sequence distribution of the monomer units in the homopolymer chains of poly(butyl- α -cyanoacrylate) nanoparticles (PBCN) [2]. The configurational and tactic arrangement of sequences can be described at triad-tetrad level.

The stereochemical sequence distribution of the monomer units was defined by analysis of their high-resolution 1D ^1H and ^{13}C NMR and 2D J-resolved, $^1\text{H}/^{13}\text{C}$ HSQC and $^1\text{H}/^{13}\text{C}$ HMBC NMR spectra. The results were verified by employment of B3LYP/6-31G(d) calculations and are consistent with the preferred tendency of polymer chains of PBCN to adopt syndiotactic placements. The proton and carbon chemical shielding were calculated at BPW91/6-31+G(2d,p) level using the GIAO approach and B3LYP/6-31G(d) optimized geometry. The present investigations show that the most favorable tetramer in PBCN should be SSRS (*rrr* triad).

References:

1. Couvreur P, Kante B, Roland M, Guiot P, et al. *J. Pharm. Pharmacol* **31**, 331–332 (1979)
2. Markova N., Ivanova G., Enchev V., Simeonova M. *Structural Chemistry* **23**, 815–824 (2012)

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