

MICROSTRUCTURE OF POLYMER NANOPARTICLES: NMR SPECTROSCOPY AND DFT CALCULATIONS

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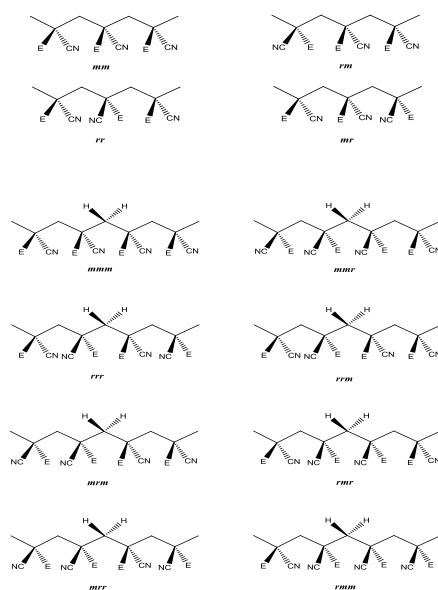
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In recent years, there has been intensive research on the development of novel multifunctional nanoparticles for biomedical and diagnostic applications. The main challenge in the design of drug delivery systems is to obtain a higher therapeutic effect with minimal toxicity, and the protection of the incorporated drugs from premature deactivation before reaching the desired site of action. It is well established that chemical and physical properties of polymers, such as biodegradability, strength of adhesion, polymer hydrophilic/hydrophobic properties and biocompatibility are directly related to their chemical structure and stereochemical sequence distribution. The knowledge of the chemical composition and microstructure of polymers and influence of these parameters on various polymer properties is important for their biomedical and diagnostic applications. Nuclear magnetic resonance spectroscopy is one of the most efficient and powerful experimental methods for evaluation of structural and stereochemical characteristics of 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) [1]. Butyl- α -cyanoacrylate-based polymers are chiral structures with asymmetric centres positioned at the main chain quaternary carbons. The microstructure of the polymer is dependent on the stereochemical configuration and arrangement of the monomer units into the polymer chains. The configurational and tactic arrangement of sequences can be described at triad-tetrad level. The possible triad and tetrad arrangements of the monomer units of PBCN are presented schematically on Scheme 1.



E=COOBu

Scheme 1. Possible triad and tetrad arrangements of the monomer units of PBCN.

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 (Fig. 1). The values of the triad and tetrad populations were determined from the relative peak intensities of the carbon resonances of OCH_2 from the side chain and CH_2 from the main polymer chains, respectively.

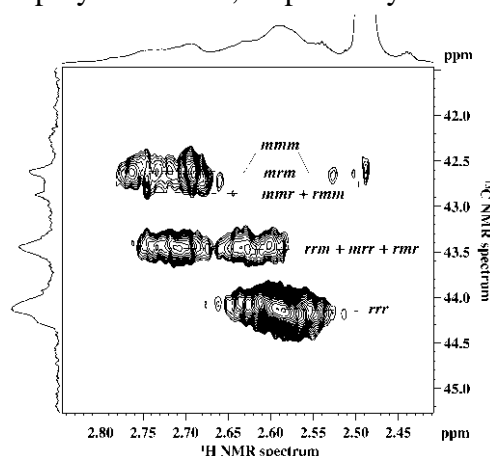


Figure 1. Selected spectral area from $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum of PBCN

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 combined NMR and quantum chemical investigations elucidate on the structure of poly(butyl- α -cyanoacrylate) and show that the most favorable tetramer in PBCN should be *rrr* (Fig. 1).

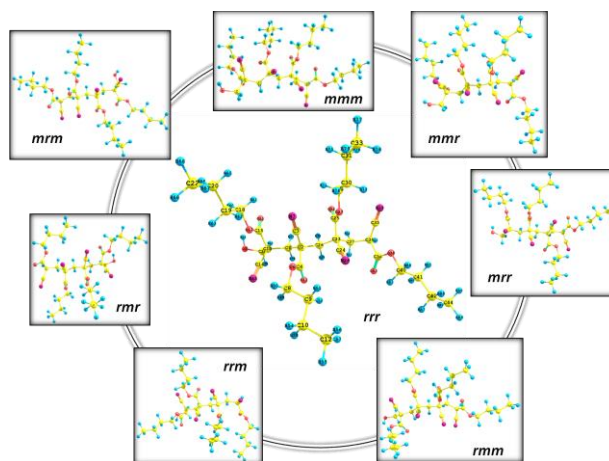


Figure 2. B3LYP/6-31G(d) optimized structures of poly(butyl- α -cyanoacrylate) tetrads.

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References

- [1] N. Markova, G. Ivanova, V. Enchev, M. Simeonova. Tacticity of poly(butyl- α -cyanoacrylate) chains in nanoparticles: NMR spectroscopy and DFT calculations. *Structural Chemistry* (2011), in press, 3DOI 10.1007/s11224-011-9928-3.