University of Fribourg / Faculty of Science and Medicine / Department of Chemistry

Towards Auxetic Materials upon Configurational Change of Aromatic Amides

Mahshid Alizadeh

The presented work focuses on exploring new approaches towards polymeric molecular auxeticity_ materials with a negative Poisson's ratio_ using molecular geometric shapes synthetically achieved via shape-persistent sequence controlled aromatic amide oligomers. oligoaramids are utilized to manifest the configurational change of *cis* to *trans* amide bond by applying force or cleavage of an *N*-protective group. To investigate the *cis-trans* configurational change in aromatic amide oligomers in solution by spectroscopy measurement, oligoaramides carrying chromophore labels were synthesized. In the *cis*-configuration, the chromophores are in close proximity to each other whereas in the *trans* configuration the distance between the chromophores is larger.

To synthesize a polymer chain in which all amide bonds are in the *cis* conformation and this amide isomer formation needs secondary amide bonds or, in other words, *N*-substituted amide bond. a polymerization condition in which phenyl 4-aminobenzoate derivatives as the monomers in presence of bifunctional initiator underwent like polycondensation reaction by addition of lithiumbis(trimethylsilyl)amide(LiHMDS)as a strong non-nucleophilic base to produce poly(p-benzamide)s with phenolate end groups. The end group of the polymer chain was confirmed by MALDI-ToF mass spectroscopy. To prove telechelicity, different end functional groups such as alkyne, amine, alcohol, alkyl halide, and olefin were used for post modification polymerization reactions. Successful end group modification was confirmed by isotopically resolved MALDI-ToF mass spectrometry. With valuable data about amide configurational change upon applying force or by cleavage of an *N*-protective group and also the synthesis of cispoly(p-benzamide)s, we are now one significant step closer to the synthesis of the desired geometric shape for auxetic behavior by using *cis-trans* aramides.

Jury:
Prof Dr. Andreas F. M. Kilbinger, (Thesis supervisor)
Prof Dr. Fabio Zobi, (Internal co-examiner)
Prof Dr. Helmut Schlaad, (External co-examiner)
Prof Dr. Marco Lattuada, (President of the committee)