AFM STUDY OF MULTIVALENT ADHESIVE PROPERTIES OF POLYMERS PREPARED BY COBALT-MEDIATED RADICAL POLYMERIZATION AND NITRONE-MEDIATED RADICAL COUPLING

Nicolas Willet (1), Damien Sluysmans (1), Cédric Delvaux (1), Antoine Debuigne (2), Christophe Detrembleur (2), Christopher Barner-Kowollik (3), Thomas Junkers (4), Anne-Sophie Duwez (1)

(1) NanoChem, Department of Chemistry, University of Liege, Sart-Tilman B6a, 4000 Liège, Belgium
(2) CERM, Department of Chemistry, University of Liege, Sart-Tilman B6a, 4000 Liège, Belgium
(3) Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
(4) Institute for Materials Research (IMO), Polymer Reaction Design Group, Universiteit Hasselt, Diepenbeek, Belgium

Well-defined poly(vinyl acetate) (PVAc) chains prepared by CMRP (cobalt-mediated radical polymerization) were coupled using an alkyne-functional nitrone via NMRC (nitrone-mediated radical coupling).[1] In all the cases, the coupling efficiencies were close to 90% or higher. The polymers mid-chain functionalized with an alkyne group were then reacted with azide-functionalized atomic force microscopy (AFM) tips via copper-catalyzed azide-alkyne cycloaddition (CuAAC). As a result, polymers having a double-branch architecture were linked to AFM tips via a short linker (see Figure 1). The structure and the molecular parameters of the polymers were determined by NMR and GPC, whereas the 'click' step onto AFM tips was assessed by performing the same CuAAC reaction onto macroscopic surfaces and characterizing them by ATR FT-IR.

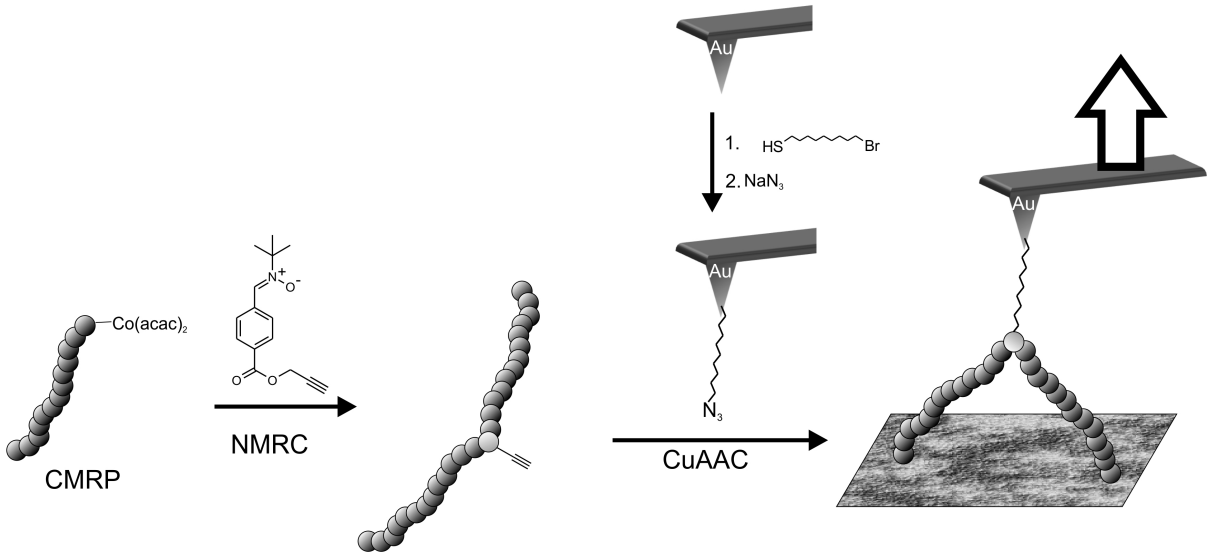

Figure 1: *Schematic representation of the synthesis of mid-chain alkyne-functionalized polymers via combination of CMRP and NMRC followed by CuAAC conjugation with an AFM tip grafted with a short azide-bearing linker. AFM SMFS was performed using such novel functional AFM cantilevers.*

The adhesive properties of these double-branched polymers were studied by AFM single-molecule force spectroscopy (SMFS). By performing approach-retraction cycles in solution upon a glass surface, the interaction between single PVAc chains and the surface was investigated. The effect of the double-branch architecture on the adhesion forces was under focus. Setting a residence time of the tip on the surface before retraction was found to have a beneficial influence on the adhesion forces. Signs of multiple interactions acting in parallel were detected in the experimental force-distance traces.

References

1) Christophe Detrembleur, Antoine Debuigne, Ozcan Altintas, Matthias Conradi, Edgar H.H. Wong, Christine Jérôme, Christopher Barner-Kowollik and Thomas Junkers, Polymer Chemistry 2012, 3 (1), 135-47