

Cis-to-Trans Isomerization of Carbon-Carbon Double Bond by Single Molecule Force Spectroscopy

¹Milad Radiom, ²Phally Kong, ¹Plinio Maroni, ²Andreas F.M. Kilbinger, ¹Michal Borkovec

¹Department of Inorganic and Analytic Chemistry, University of Geneva, Sciences II, 30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland

²Department of Chemistry, University of Fribourg, Chemin du Musée 9, 1700 Fribourg, Switzerland
milad.radiom@unige.ch

Abstract There are numerous examples of carbon-carbon double bond containing molecules that are frequently used in chemistry, biology, and medicine. One major attribute of these molecules is that they normally have two isomerization states, namely *cis* and *trans*, while each isomer presents specific physical, chemical and pharmacological properties. The isomerization of double bond (*cis* to *trans* and the reverse reaction) is induced in nature and technology via irradiation, thermally or by catalysts. The most notable example is the photo-induced *cis*-to-*trans* isomerization of 11-*cis*-retinal to all-*trans*-retinal and the subsequent reverse reaction that is enzymatic. So far the effect of mechanical force on isomerization of double bond has not been investigated. This is while mechanical force has been used as an alternative trigger to induce transitions in various bonding systems such as coordination, complexation, hydrogen bonding and covalent bonds. Here we present our results on force-induced *cis*-to-*trans* isomerization of double bond at the level of single polymer molecules containing *cis* double bond using atomic force microscopy (AFM). Three double bond containing polymers were used, namely **P1**, *cis*-**PB** and **PB**. As control, three exclusively single bond containing polymers were investigated, namely **P2**, **PE** and **PS**. The structures of these polymers are shown in figure 1. Upon stretching *cis* double bond containing polymers to elevated forces, a sudden relaxation in force and increase in elongation of polymer was observed that is attributed to isomerization (figure 2). Investigation of exclusively single bond containing polymers did not show any trace of isomerization. Our results revealed an isomerization force of 800 ± 60 pN (figure 3). This force is slightly lower than the force associated with breaking of covalent bonds and rings ~ 1 -2 nN [2,3]. Our results show that the mechanical force can be used to trigger isomerization of double bond. Our results also open the possibility of a new class of force-responsive polymers based on mechano-isomerization of double bond.

References

- [1] M. K. Beyer and H. Clausen-Schaumann, *Chemical Reviews*, **8** (2005) 2921.
[2] J. Wang, *et al.*, *Nature Chemistry*, **7** (2015) 323.
[3] M. Grandbois, *et al.*, *Science*, **283** (1999) 1727.

Figures

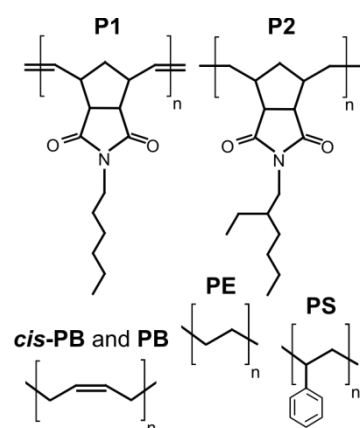


Figure 1: Structural formulas of the polymers used in this study: synthesized polymers **P1** and **P2**, *cis*-1,4-polybutadiene (**cis-PB**, *cis* 98%, *trans* 1%, vinyl 1%), 1,4-polybutadiene (**PB**, *cis* 36%, *trans* 55%, vinyl 9%), polyethylene (**PE**) and polystyrene (**PS**).

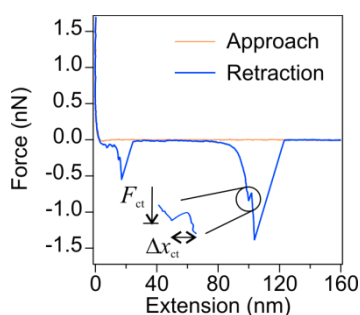


Figure 2: Force versus extension of **P1** showing an isomerization event. The onset of isomerization is denoted by force F_{ct} and elongation change Δx_{ct} .

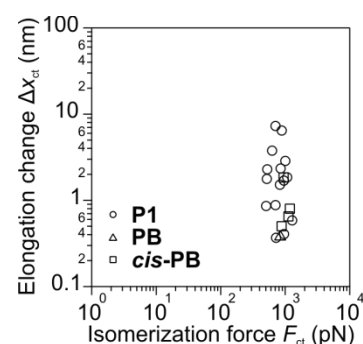


Figure 3: The elongation change Δx_{ct} of **P1**, **PB**, and **cis-PB** as a function of the isomerization force F_{ct} .