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KEYNOTE FORUM | DAY 1

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## Length scales and dynamics of polymers in solutions and solids probed by pyrene excimer formation

Fluorescence resonance energy transfer (FRET) is certainly the first fluorescence-based technique that comes to mind to probe the length scales and dynamics of macromolecules in solution and the solid state. Although not much advertised, FRET has a number of drawbacks, however, particularly the dependency of the FRET efficiency on both the internal dynamics of the macromolecule and the distribution of distances between every donor and acceptor pair. Due to the mathematical complexity of sorting through both unknown macromolecular dynamics and unknown distribution of distances between donors and acceptors, FRET measurements conducted on macromolecules in solution usually focus on macromolecules that have been labeled by a single energy donor and a single energy acceptor separated by a single contour length. This requirement implies that FRET studies generally focus on fluorescently end-labeled monodisperse linear chains where the end-to-

end distance distribution can be approximated by a Gaussian distribution. The FRET data retrieved with more complex macromolecular architectures is usually treated qualitatively. By contrast, recent developments in the analysis of fluorescence data acquired with pyrene-labelled macromolecules suggest that the average rate constant  $\langle k \rangle$  of pyrene excimer formation (PEF), where a pyrene excimer is the result of the encounter between an excited and a ground-state pyrene, is equal to the product of a bimolecular rate constant  $k_{diff}$  for diffusive pyrene-pyrene encounters times the local pyrene concentration  $[Py]_{loc}$ . The fact that PEF occurs solely on contact between two pyrene labels eliminates the complexity of dealing with constantly moving donor and acceptor labels that require that the distance distribution between donors and acceptor be continuously monitored in a FRET experiment. This insight has been recently harnessed to provide quantitative information about the internal dynamics and the length scales encountered in highly branched macromolecules such as dendrimers, polymeric bottle brushes, and arborescent polymers. This presentation



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will describe how PEF data are acquired and interpreted in order to provide such information on virtually any type of macromolecule in solution.

### Biography

Jean Duhamel after being trained as a chemical engineer in France at the Ecole Nationale Supérieure des Industries Chimiques, he obtained in Ph.D. in 1989 under the supervision of Dr. André at the Institut National Polytechnique de Lorraine (France). Following a first post-doc at the University of Toronto with Prof. Winnik and a second one at the University of Pennsylvania with Prof. Lu, he joined the University of Waterloo in 1996. Over the past 20+ years, work from his research group has aimed to establish the versatility of pyrene excimer fluorescence or PEF to probe the dynamics, conformation, and interactions of any macromolecule in solution. He has published over 100 refereed papers to date with close to half of them having been published in *Macromolecules*, the top scientific journal for macromolecular science.

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