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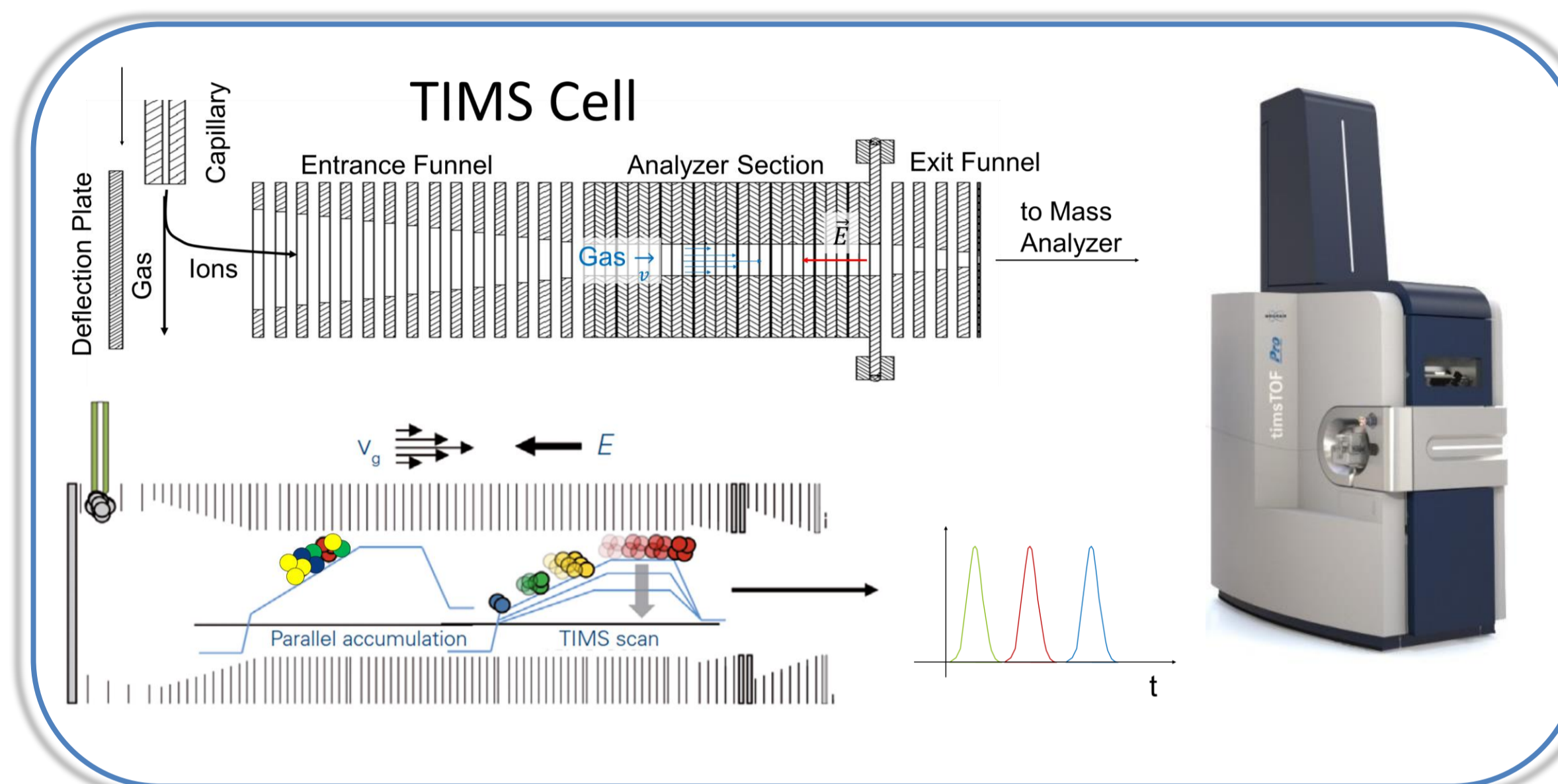
## Introduction

The physical properties of polymer materials are greatly affected by the primary structure of the polymer chains that make up the material. Therefore, the development of a synthetic method for controlling the primary structure and the development of an analytical technique to elucidate the structure are important issues.

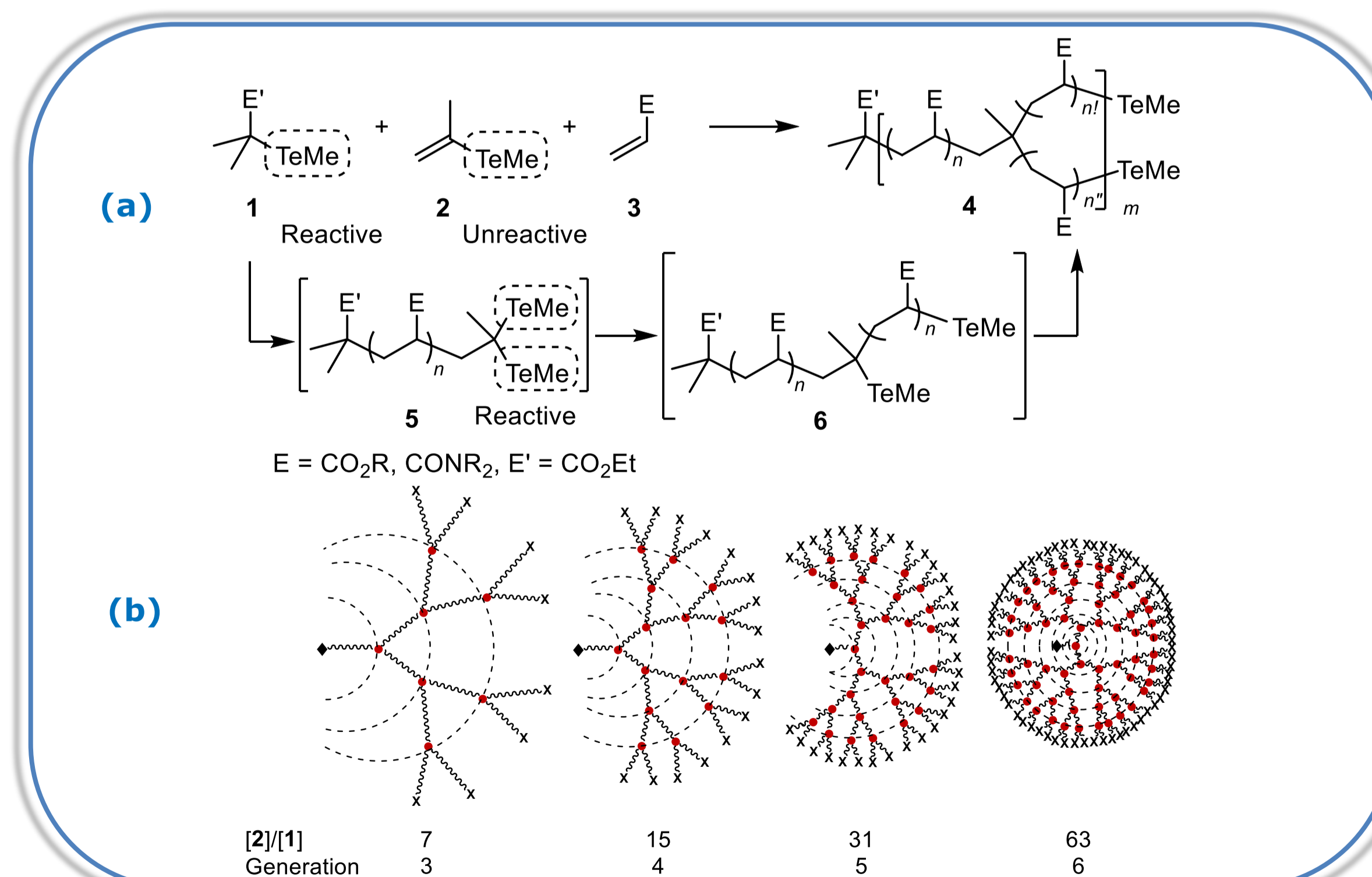
In this study, novel synthetic methods for the polymerization of controlled and highly branched PMMAs and the polymerization of acrylamides with dual control of molecular weight and stereoselectivity were developed (Figure 2). For the first time, trapped ion mobility mass spectrometry (Figure 1) was used to determine both the effect of the branching structure on the molecular volume of highly branched PMMA and the effect of tacticity on the polymer structure of PDEAA in the gas phase.

## Methods

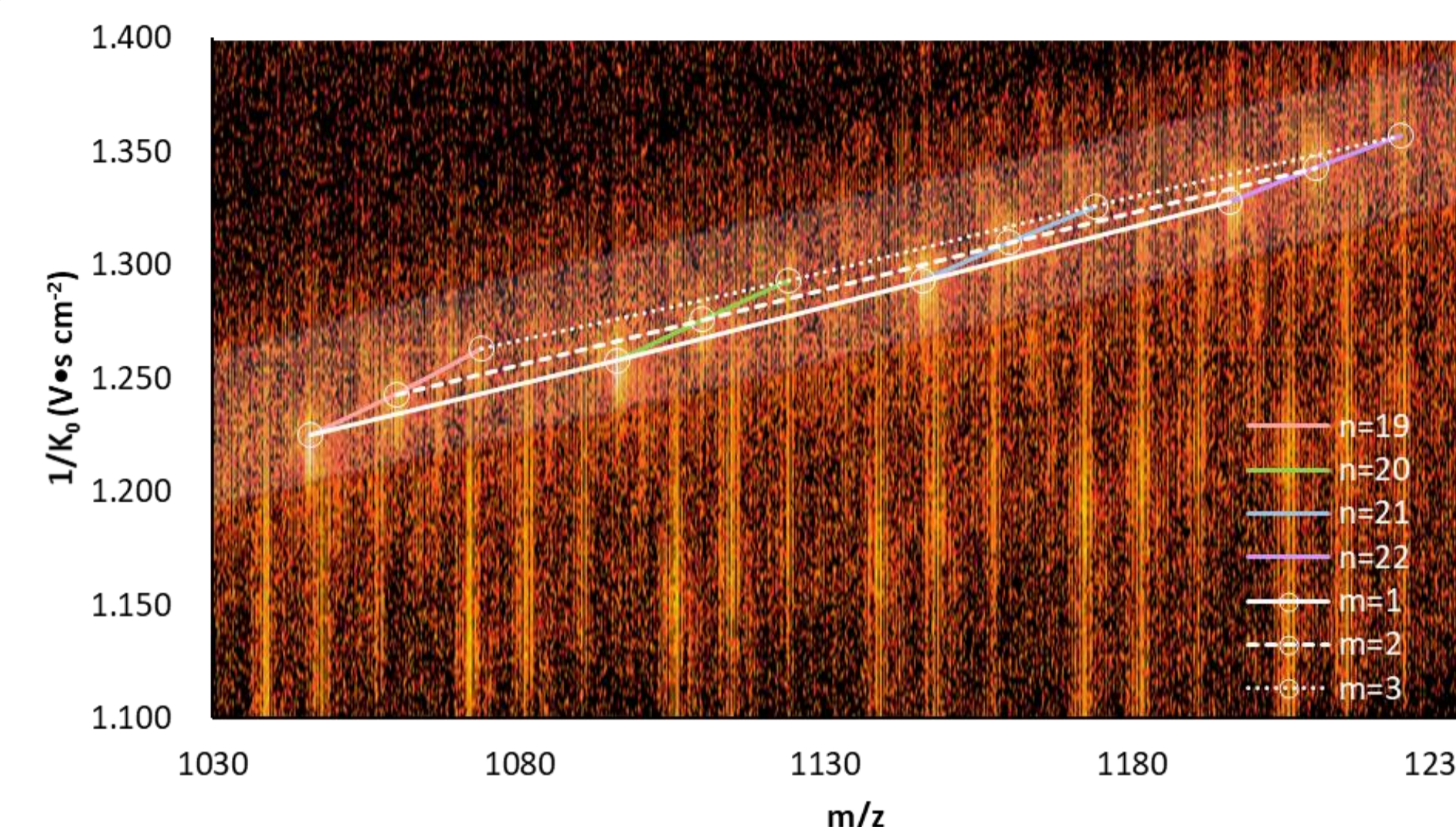
- A Bruker microflex MALDI-TOF mass spectrometer, equipped with a nitrogen laser was used in positive reflector mode with 20 kV acceleration voltages for the analysis of highly branched polymethacrylates.
- A Bruker timsTOF mass spectrometer was used in positive ion mode with an electrospray ionization (ESI) method for the analysis of the controlled branching structures of polydimethylmethacrylate (PMMA) and the tacticity of polydiethylacrylamide (PDEAA).
- The polymer samples were dissolved in methanol or THF (0.50 mL, 0.050 mgmL<sup>-1</sup>) and an aqueous solution of sodium trifluoroacetate (25  $\mu$ L, 0.50 mg mL<sup>-1</sup>) was added as the cationization agent prior to analysis.



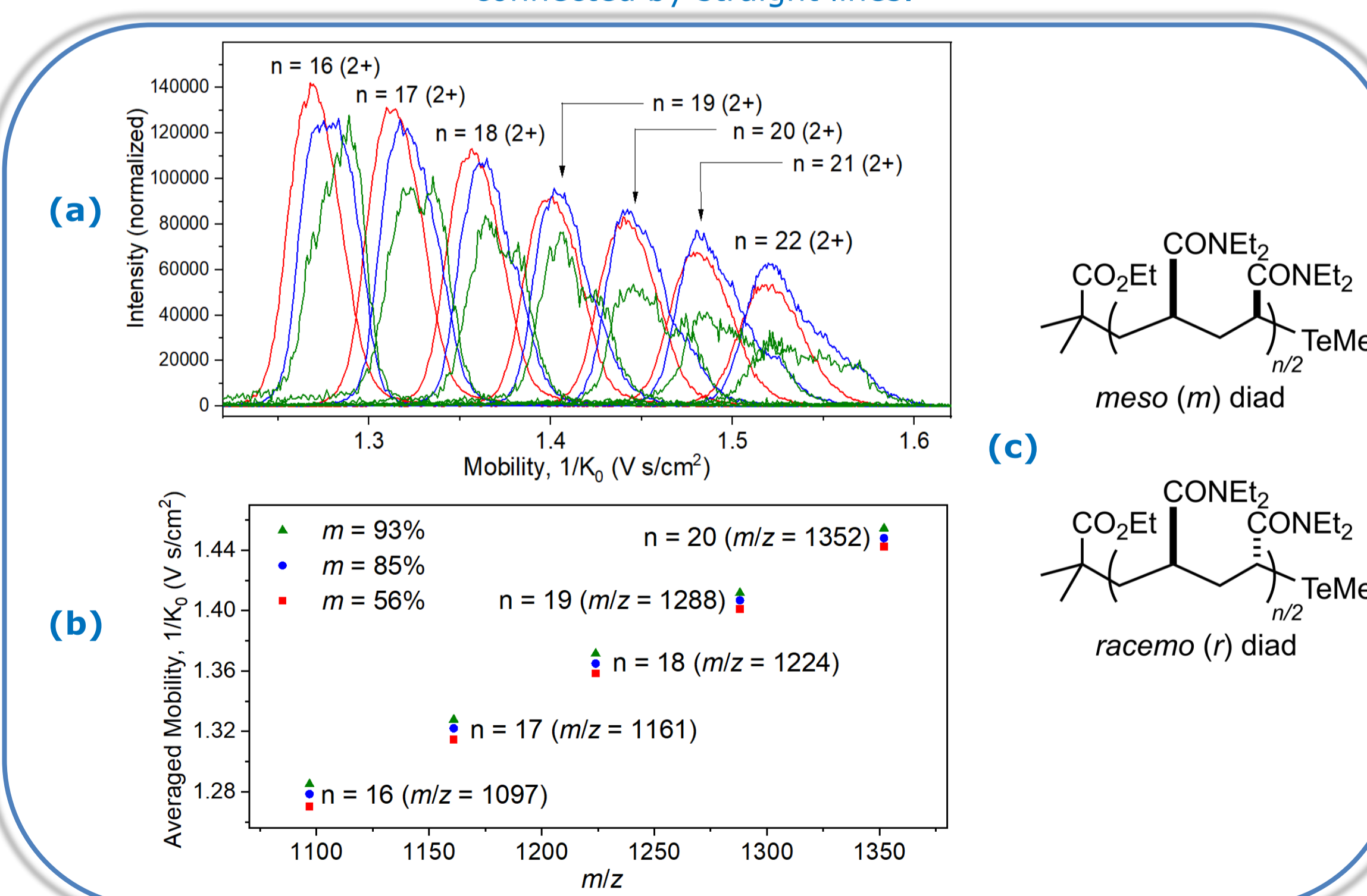
**Fig. 1:** Schematic representation of TIMS components and general principles of operation.



**Fig. 2:** (a) Synthesis of highly branched PMMAs by the copolymerization of MMA and 2 vinyl monomers. (b) Schematic structures of ideal polymer products obtained by the method in (a).



**Fig. 3:** Heat map of selected mass region of HB-PMMA with branching unit  $m = 1-3$  and MMA unit  $n = 19-22$ . The signals having the same repeating units  $m$  and  $n$  are connected by straight lines.



**Fig. 4:** Ion mobility spectrometry of PDEAAs with different  $m$  diad selectivities (red: 56%, blue: 85%, green: 93%). (a) Ion mobility and peak intensities and (b) the correlation between ion mobility and  $m/z$ . (c) Structures of PDEAAs

## Results

The effect of the branching structure on the molecular volume of the synthesized PMMAs in the gas phase was clarified by trapped ion mobility spectroscopy (TIMS)-TOF MS measurements, which reveals that the collisional cross section of ionized PMMA increases with increasing branching numbers (Figure 3).

The effect of tacticity on the polymer-chain structure in the gas phase was also clarified for the first time using trapped ion mobility mass spectrometry and revealed that the mobility increased as the  $m$  diad selectivity increased among the PDEAAs having the same repeating unit in all cases (Figure 4).

The observed effect of tacticity on the polymer-chain structure in the gas phase was identical to those observed in a solution and could be explained by the increase of stretching of the polymer main chain as the  $m$  diad selectivity increased.

## References

- Lu, Y.; Yamago, S., *Macromolecules* 2020, 53, 3209.
- Imamura, Y.; Fujita, T.; Kobayashi, Y.; Yamago, S. *Polym. Chem.* 2020, 11, 7042..

## Conclusions

- Novel synthetic methods for the polymerization of controlled and highly branched PMMAs and the polymerization of acrylamides with dual control of molecular weight and stereoselectivity were developed.
- For the first time, trapped ion mobility mass spectrometry was used to determine both the effect of the branching structure on the molecular volume of highly branched PMMA and the effect of tacticity on the polymer structure of PDEAA in the gas phase.
- These studies will broaden the synthetic toolbox for the design and characterization of novel complex but precise macromolecular structures and their applications.