# Supporting Information

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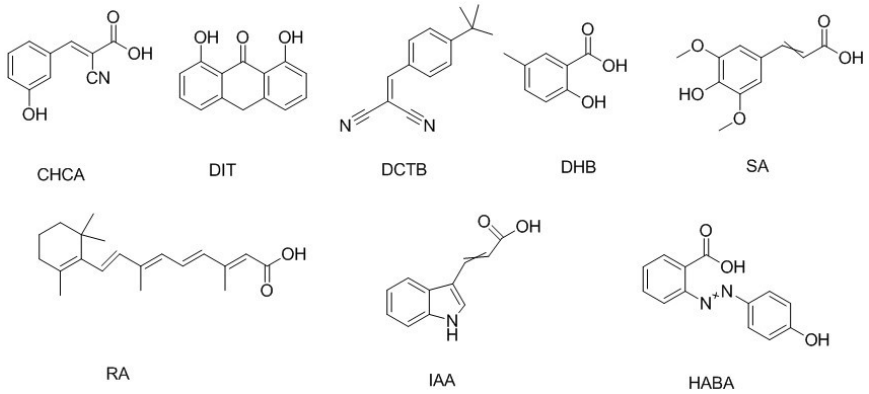
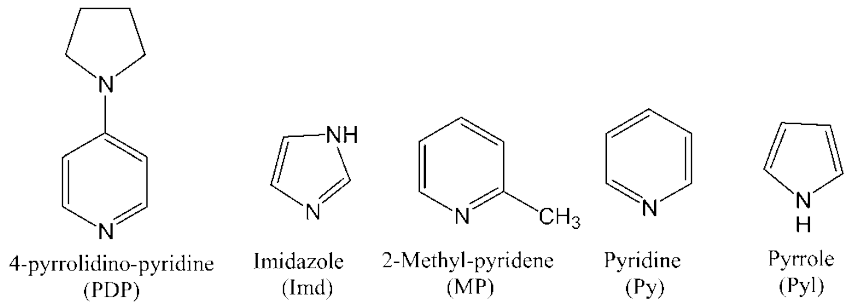
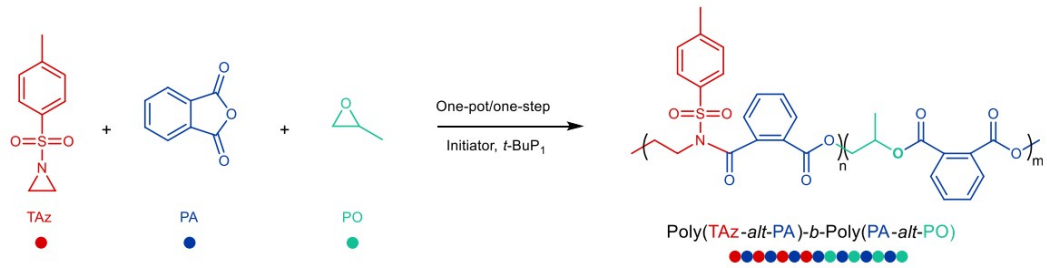



**Scheme S1**. The chemical structures of some common MALDI matrices.




**Scheme S2.** Structures of N-heterocyclic molecules, investigated as initiators for ROP of lactide. Reprinted with permission from ref. 130.




**Scheme S3.** Terpolymerizations of TAz, PA, and PO. The synthesis of diblock dialternating terpolymers with a sharp boundary instead of a tapered sequence at the conjunction between the two alternating blocks. Reprinted with permission from ref. 133.

**Table S1**. The structures and types of the synthetic homopolymers commonly used for the MALDI-TOF-MS analyses

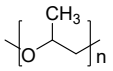
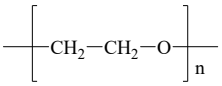
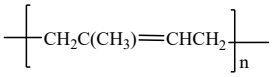
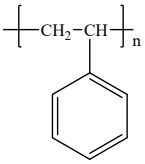
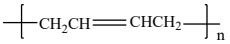
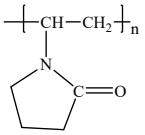
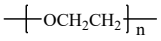
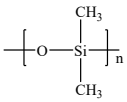
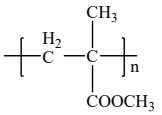
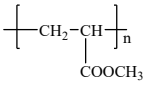
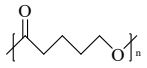
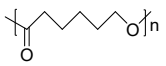
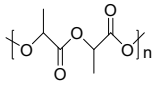
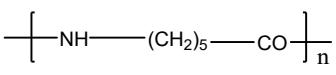
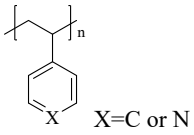
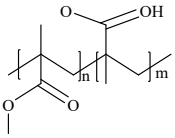
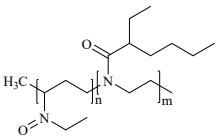
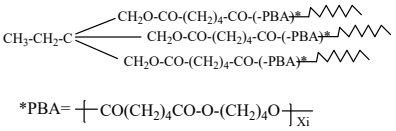
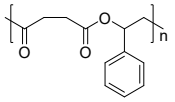
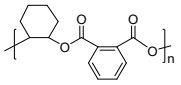
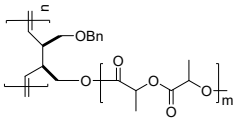
| No. | polymer | Symbol | Structure |
|---|---|---|---|
| 1 | polypropylene glycol | PPG |  |
| 2 | poly(ethylene glycol) | (PEG) |  |
| 3 | polyisoprene | PIP |  |
| 4 | polystyrene | PS |  |
| 5 | polybutadiene | PB |  |
| 6 | polyvinylpyrrolidone | PVP |  |
| 7 | poly(ethylene oxide) | PEO |  |
| 8 | poly(dimethyl siloxane) | PDMS |  |
| 9 | poly(methylmethacrylate) | PMMA |  |
| 10 | poly (methyl acrylate) | PMA |  |
| 11 | poly (δ-valerolactone) | PVL |  |
| 12 | Poly(ε-caprolactone) | PCL |  |
| 13 | Poly(lactic acid) | PLA |  |
| 14 | Nylon-6 | Ny6 |  |

**Table S2.** The structures and types of the synthetic copolymers commonly used for the

MALDI-TOF-MS analyses

| No. | polymer | Symbol | Structure |
|---|---|---|---|
| 1 | poly(styrene-co-4-vinylpyridine) | P(S-4VP) |  X=C or N |
| 2 | polymethyl methacrylate-co-methacrylic acid | (PMMA-co-MAA) |  |
| 3 | poly (2-oxazoline) | P(EtOx-b-EPOx) |  |
| 4 | hybrid poly (butylene adipate) copolymers | HPBA |  |
| 6 | poly (styrene oxide-*alt*- succinic anhydride) | P(SO-*alt*-SA) |  |
| 7 | poly (phthalic anhydride-*alt*-cyclohexane oxide) | P(PA-*alt*-CHO) |  |
| 8 | poly(1,4-butadiene)-graft-poly(L-lactide) | $PBu_n$-g-$P_LLA_m$ |  |

## Kendrick analysis

The Kendrick analysis adds a second dimension to the mass spectrum through the evaluation of the "fractional parts" of the accurately mass measured *m/z* values. The fractional part of *m/z* contains information about the elemental composition of the associated ions. Plotting the fractional parts of *m/z* as a function of *m/z*, while at the same time retaining the intensity of the associated peaks via colour coding or point size, produces a two-dimensional map of the mass spectrum[1]. It can help us to explore the complex mass spectral data or filtering the unwanted signal.

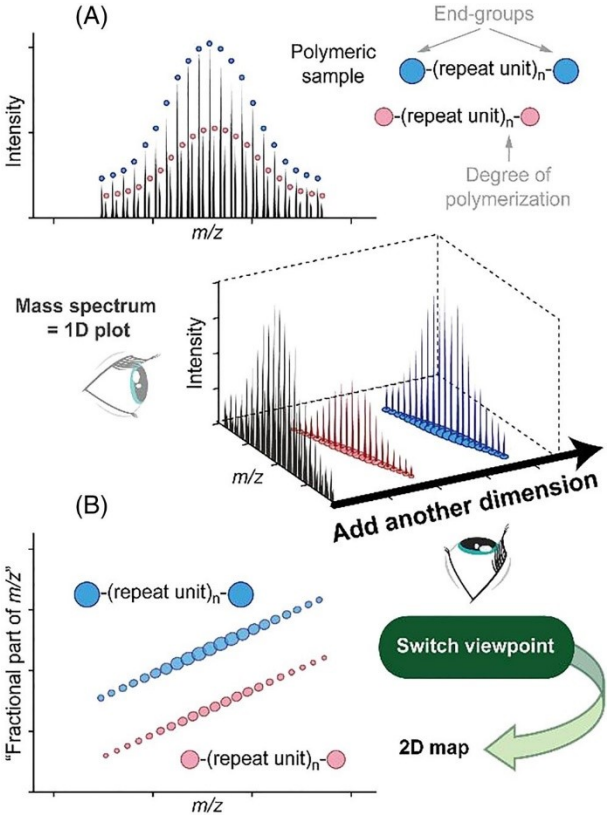



**Fig. S1** Generic representation of the change in viewpoint from a one-dimensional mass spectrum to a two-dimensional Kendrick plot. Reprinted with permission from ref. 79.