Copolymer microstructure determination by the click of a button; reactivity ratios of comonomers from a single MALDI-ToF-MS measurement.

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Experimental Section

Reagents. Free radical: Monomers were purified by conventional methods. 2,2’-azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. 1-Dodecanethiol (DDT) was used without further purification and purchased from Aldrich. Ring opening: 1,5- dioxepan-2-one and 4-methylcaprolactone were prepared according to literature procedures. D-Lactide was a gift from Purac. ε-Caprolactone, δ-Valerolactone and Tin (II) 2-ethylhexanoate (Sn(Oct)₂) was purchased from Aldrich. The data of the copolymerization of trimethylene carbonate and ε-caprolactone are reported elsewhere.

Synthesis. Free radical: A mixture of comonomers (6 mmol) in required molar ratio, initiator AIBN and chain transfer agent DDT (in a molar ratio of 500:10:1 respectively) was reacted in a 1.5 mL crimp lid vial placed in an aluminium heating block at 60 or 70 °C. Crude samples were taken with an interval of 30 s to undergo immediate MALDI-ToF-MS analyses. Ring opening: A mixture of comonomers (10 mmol) in required molar ratio and a drop of Sn(Oct)₂ was reacted in a 1.5 mL crimp lid vial placed in an aluminium heating block at 130 °C. Crude samples were taken with an interval of 5 minutes to undergo immediate MALDI-ToF-MS analyses.

MALDI-ToF-MS Analysis. MALDI-ToF-MS analysis was performed on a Voyager DE-STR from Applied Biosystems equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. Mass spectra of 1000 shots were accumulated. The polymer samples were dissolved in THF at a concentration of 1 mg mL⁻¹. The cationization agent used was potassium trifluoroacetate (Fluka, >99%) dissolved in THF at a concentration of 5 mg mL⁻¹. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg mL⁻¹. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the reflectron mode as well as the linear mode.

Benchmark tests

Benchmark tests were performed to determine the number of time, ‘d’, a single chain requires to be simulated by MC to obtain an acceptable absolute error. These tests were performed for a Bernoullian distribution since the analytical expression for the probability density function is known, enabling direct comparison with the chemical composition distribution determined by MC. Evidently, the computer’s processor time increases but the absolute error decreases with increasing sample size as shown in Figure S1. In the case of a quad core processor the time required to simulate a chain $3 \cdot 10^6$ times is 5 s with an accuracy that allows for three digits.

Figure S1a. Benchmark Dell PC, 1 CPU, 3GHz processor, 1 Gb RAM.
Figure S1b. Benchmark LIME PC, 4 CPUs parallel, 3 GHz processor, 8 Gb RAM.
Flow chart of procedure to determine r-values.

**Flowchart of procedure to determine reactivity ratios by MALDI-ToF-MS.**

1. **Polymerization**
2. **MALDI-ToF-MS**
   - Deconvolution MALDI-ToF-MS spectrum into matrix
   - Extract chemical composition distribution per chain length
     - MC simulation of 1st order Markov chain for chain length 'n' starting with $P_{11} + P_{22} = 1$
     - Change $P_{11}$ and $P_{22}$ in order to minimize LSSQ and simulate new 1st order Markov Chain by MC
     - Check if measured distribution fits MC simulated distribution by LSSQ
       - NO
       - YES
         - Calculate r-values from feed ratios and P-values
   - MATLAB

**Figure S3.** Flowchart of procedure to determine reactivity ratios by MALDI-ToF-MS.
Classification of reactivity ratios according to topology.

Table S1 is given here as a support to how the reactivity ratios relate to the expected microstructure of the copolymer.

**Table S1. Classification of reactivity ratios and microstructure.**

<table>
<thead>
<tr>
<th>Ratios</th>
<th>Topology</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1 = 1/r_2$, $r_2 = 1/r_1$</td>
<td>Random copolymer</td>
</tr>
<tr>
<td>$r_1 &lt;&lt; 1$, $r_2 &lt;&lt; 1$ ($r_1 r_2 \to 0$)</td>
<td>Alternating copolymer</td>
</tr>
<tr>
<td>$r_1 &gt;&gt; 1$, $r_2 &lt; 1$ ($r_1 r_2 &lt; 1$)</td>
<td>Tends to homopolymer of $M_i$</td>
</tr>
<tr>
<td>$r_1 &gt;&gt; 1$, $r_2 &gt;&gt; 1$</td>
<td>Tends to block copolymer</td>
</tr>
</tbody>
</table>

The analytical form of the probability mass function:

The probability mass function of the number of monomers of type 1 (= monomer B), in a copolymer consisting of monomers A and B with a length $n$ is given.

$$P_a(N_1(n) = m)$$  \hspace{1cm} (1)

Where $n$ is the chain length, $m$ the number of B units in the chain and $P_a$ is the probability distribution.

In order compute a probability mass function, the Fourier theory shall be used. It is already mentioned in an internal memo that the Fourier theory can be very convenient to compute such mass functions. Let $f : \mathbb{N} \to \mathbb{R}$

$$\hat{f}(k) = \sum_{x=0}^{\infty} e^{ikx} f(x) = \sum_{x=0}^{\infty} \cos(kx) f(x) + i \sum_{x=0}^{\infty} \sin(kx) f(x)$$  \hspace{1cm} (2)

And for the Fourier inverse:

$$f(x) = \int_{-\pi}^{\pi} e^{-ikx} \hat{f}(k) \frac{dk}{2\pi}$$  \hspace{1cm} (3)

Now we would like to apply these to formulas to calculate our mass probability function. The characteristic function of $N_1(n)$ is now given by:

$$\hat{f_a}(k) = \sum_{m=0}^{n} e^{im} P_a(N_1(n) = m)$$  \hspace{1cm} (4)
In order to help the reader we shall apply these formulas for a polymer with chain length equals three (n=3). Therefore we go back to “tree” of probabilities as depicted below.

R is our starting group (e.g. a radical). Every time a chain end reacts there will be 2 possibilities, simply an attachment of repeat unit A or B. All probabilities are now given by all the possible paths we can take. In this case at a chain length of m=3, 8 possible routes could have been taken. The probability for each route is given by the product of the probabilities. For example, the probability of 3 A units in a row is \((pa0)(pa)(pa)\) etc. The next step is that we write the sum of probabilities for chains which have the same number of B monomers (m) for a given chain length (n).

\[
\begin{align*}
\text{m=0} & \quad (pa0)(pa)^2 \\
\text{m=1} & \quad (pa0)(pa)(1-pa) + (pa0)(1-pa)(1-pb) + (pb0)(1-pb)(pa) \\
\text{m=2} & \quad (pa0)(1-pa)(pb) + (pb0)(1-pb)(1-pa) + (pb0)(pb)(1-pb) \\
\text{m=3} & \quad (pb0)(pb)^2
\end{align*}
\]
Applying the following formula, we obtain:

\[
\hat{f}_a(k) = \sum_{m=0}^{3} e^{ikm} p_a(N_1) = m
\]

\[
= e^{ik_0} (pa0)(pa) + e^{ik_1} (pa0)(1 - pa) + (pa0)(1 - pa)(1 - pb) + (pb0)(1 - pb)(pa) + e^{ik_2} (pa0)(1 - pa)(pb) + (pb0)(1 - pb)(1 - pa) + (pb0)(pb)(1 - pb) + e^{ik_3} (pb0)(pb)^2
\]

This result can be written in a more compact and general way by introducing it in a matrix form.

\[
\hat{f}_a(k) = \sum (pa0) \ (pb0) e^{ik} \left( \frac{pa}{(1 - pb)} \ (1 - pa)e^{ik} \right)^{n-1}
\]

Now the Fourier inverse rather easy:

\[
P_a(N_1) = m = \int_{-\pi}^{\pi} e^{-ikm} \sum (pa0) \ (pb0) e^{ik} \left( \frac{pa}{(1 - pb)} \ (1 - pa)e^{ik} \right)^{n-1} \frac{dk}{2\pi}
\]

This is finally the general formula that is used to perform all other calculations and more over this formula is explicit!

Note that \( pa = P_{11}, \ pb = P_{22}, \ pa0 = P_{11}0 \) and \( pb = P_{22}0 \)
MALDI-ToF-MS spectra

The MALDI-ToF-MS spectra recorded in the reflector mode and the matching isotope patterns for end group determination are given in the following section. First, the spectra of the free radical copolymers and second the spectra of the ring opening copolymers will be shown. Table 2 is given as support to explain the difference between peaks in the spectra.

Table S2. Molecular weights of monomers.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name</th>
<th>Mw (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>Butyl Acrylate</td>
<td>128</td>
</tr>
<tr>
<td>MA</td>
<td>Methyl Acrylate</td>
<td>86</td>
</tr>
<tr>
<td>EA</td>
<td>Ethyl Acrylate</td>
<td>100</td>
</tr>
<tr>
<td>nBMA</td>
<td>n-Butyl Methacrylate</td>
<td>142</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl Methacrylate</td>
<td>100</td>
</tr>
<tr>
<td>EMA</td>
<td>Ethyl Methacrylate</td>
<td>114</td>
</tr>
<tr>
<td>Sty</td>
<td>Styrene</td>
<td>104</td>
</tr>
<tr>
<td>VAc</td>
<td>Vinyl Acetate</td>
<td>86</td>
</tr>
<tr>
<td>CL</td>
<td>ε-Caprolactone</td>
<td>114</td>
</tr>
<tr>
<td>D-LA</td>
<td>D-Lactide</td>
<td>144</td>
</tr>
<tr>
<td>DXO</td>
<td>1,5-dioxepan-2-one</td>
<td>116</td>
</tr>
<tr>
<td>MCL</td>
<td>4-Methylcaprolactone</td>
<td>128</td>
</tr>
<tr>
<td>TMC</td>
<td>Trimethylene carbonate</td>
<td>102</td>
</tr>
<tr>
<td>VL</td>
<td>δ-Valerolactone</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure S3. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of styrene/methyl acrylate.

Figure S4. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of styrene/ethyl acrylate.
Figure S5. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of styrene/butyl acrylate.

Figure S6. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of styrene/methyl methacrylate.
Figure S7. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of styrene/ethyl methacrylate.

Figure S8. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of styrene/butyl methacrylate.
Figure S9. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of methyl methacrylate/ethyl methacrylate.

Figure S10. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of methyl methacrylate/butyl methacrylate.
Figure S11. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of methyl methacrylate/butyl acrylate.

Figure S12. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of methyl methacrylate/vinyl acetate.
Figure S13. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of butyl methacrylate/ethyl acrylate.

Figure S14. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of ethyl acrylate/vinyl acetate.
**Figure S15.** Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of vinyl acetate/butyl acrylate.
Figure S16. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of ε-caprolactone/4-methylcaprolactone recorded in reflector mode with Na⁺.

Figure S17. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of ε-caprolactone/1,5-dioxepan-2-one recorded in reflector mode with K⁺.
Figure S18. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of δ-valerolactone/1,5-dioxepan-2-one recorded in reflector mode with K⁺.

Figure S19. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum of the copolymer of ε-caprolactone/trimethylene carbonate with 1,3-propanediol as initiator recorded in reflector mode with K⁺.
Figure S20. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum the copolymer of lactide/1,5-dioxepan-2-one recorded in reflector mode with K⁺.

Figure S21. Experimental (full and zoomed in, top) and simulated (bottom) MALDI-ToF-MS spectrum the copolymer of ε-caprolactone / lactide recorded in reflector mode with K⁺.
Chemical composition distribution

An example of a recorded chemical composition distribution for a certain chain length will be shown for each comonomer pair treated in this paper along with the fitted distribution for that chain length.

Figure S22. Copolymer styrene/methyl acrylate, chain length 20, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

Figure S23. Copolymer styrene/ethyl acrylate, chain length 20, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
**Figure S24.** Copolymer styrene/butyl acrylate, chain length 20, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

**Figure S25.** Copolymer Styrene / Methyl methacrylate, chain length 20, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
Figure S26. Copolymer styrene/ethyl methacrylate, chain length 16, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

Figure S27. Copolymer styrene/butyl methacrylate, chain length 15, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
Figure S28. Copolymer methyl methacrylate/ethyl methacrylate, chain length 17, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

Figure S29. Copolymer methyl methacrylate/butyl methacrylate, chain length 15, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
Figure S30. Copolymer methyl methacrylate/butyl acrylate, chain length 20, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

Figure S31. Copolymer methyl methacrylate/vinyl acetate, 20:80 ratio, chain length 18, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
Figure S32. Copolymer butyl methacrylate/ethyl acrylate, chain length 19, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

Figure S33. Copolymer ethyl acrylate/vinyl acetate, chain length 15, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
**Figure S34.** Copolymer butyl acrylate/vinyl acetate, chain length 30, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
Figure S35. Copolymer ε-caprolactone/4-methylcaprolactone, 50:50 ratio, chain length 18, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

Figure S36. Copolymer ε-caprolactone/4-methylcaprolactone, 30:70 ratio, chain length 18, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
Figure S37. Copolymer ε-caprolactone/1,5-dioxepan-2-one, 50:50 ratio, chain length 20, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.

Figure S38. Copolymer ε-caprolactone/1,5-dioxepan-2-one, 70:30 ratio, chain length 18, chemical composition distribution fitted using Monte Carlo simulations and measured chemical composition distribution.
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**Figure S42.** Copolymer ε-caprolactone/lactide, chain length 30, chemical composition distribution fitted using MC and measured chemical composition distribution.
Composition versus chain length

50 STY/50 MA

Figure S43. Composition vs. chain length of copolymer styrene/methyl acrylate, 50:50 ratio.

50 STY/50 EA

Figure S44. Composition vs. chain length of copolymer styrene/ethyl acrylate, 50:50 ratio.
**Figure S45.** Composition vs. chain length of copolymer styrene/butyl acrylate, 50:50 ratio.

**Figure S46.** Composition vs. chain length of copolymer styrene/methyl methacrylate, 50:50 ratio.
**Figure S47.** Composition vs. chain length of copolymer styrene/ethyl methacrylate, 50:50 ratio.

**Figure S48.** Composition vs. chain length of copolymer methyl methacrylate/ethyl methacrylate, 50:50 ratio.
**Figure S49.** Composition vs. chain length of copolymer methyl methacrylate/butyl methacrylate, 50:50 ratio.
**Figure S50.** Composition vs. chain length of copolymer methyl methacrylate/vinyl acetate, 20:80 ratio.

**Figure S51.** Composition vs. chain length of copolymer butyl methacrylate/ethyl acrylate, 50:50 ratio.
**Figure S52.** Composition vs. chain length of copolymer ethyl acrylate/vinyl acetate, 50:50 ratio.

![Graph showing composition vs. chain length for 50 VAc/50 BA copolymer](image)

**Figure S53.** Composition vs. chain length of copolymer butyl acrylate/vinyl acetate, 50:50 ratio.
**Fig S54.** Composition vs. chain length of copolymer ε-caprolactone/4-methylcaprolactone, 50:50 ratio.

**Fig S55.** Composition vs. chain length of copolymer ε-caprolactone/4-methylcaprolactone, 30:70 ratio.
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**Figure S57.** Composition vs. chain length of copolymer \( \varepsilon \)-caprolactone/1,5-dioxepan-2-one, 70:30 ratio.

**Figure S58.** Composition vs. chain length of copolymer \( \delta \)-valerolactone/1,5-dioxepan-2-one, 50:50 ratio.
Figure S59. Composition vs. chain length of copolymer ε-caprolactone/trimethylene carbonate, 50:50 ratio.
Figure S60. Composition vs. chain length of copolymer lactide/1,5-dioxepan-2one, 50:50 ratio.

**50 eCL/50 LA**

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Figure S61. Composition vs. chain length of copolymer ε-caprolactone/lactide, 50:50 ratio.

**Homo-probabilities versus chain length**

‘Most abundant chain lengths’
**Figure S62.** Homo-probabilities vs. chain length of copolymer styrene/methyl acrylate.

![Graph of STY/MA](image)

**Figure S63.** Homo-probabilities vs. chain length of copolymer styrene/ethyl acrylate.

![Graph of STY/EA](image)
**Figure S64.** Homo-probabilities vs. chain length of copolymer styrene/butyl acrylate.

**Figure S65.** Homo-probabilities vs. chain length of copolymer styrene/ethyl methacrylate.
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Figure S67. Homo-probabilities vs. chain length of copolymer methyl methacrylate/ethyl methacrylate.
**Figure S68.** Homo-probabilities vs. chain length of copolymer methyl methacrylate/butyl methacrylate.

**Figure S69.** Homo-probabilities vs. chain length of copolymer methyl methacrylate/butyl acrylate.
Figure S70. Homo-probabilities vs. chain length of copolymer vinyl acetate/methyl methacrylate.

Figure S71. Homo-probabilities vs. chain length of copolymer ethyl acrylate/butyl methacrylate.
Figure S72. Homo-probabilities vs. chain length of copolymer ethyl acrylate/vinyl acetate.
Figure S73. Homo-probabilities vs. chain length of copolymer $\varepsilon$-caprolactone/4-methyl caprolactone, 50:50 ratio.
**Figure S74.** Homo-probabilities vs. chain length of copolymer ε-caprolactone/1,5-dioxepan-2-one, 50:50 ratio.

**Figure S75.** Homo-probabilities vs. chain length of copolymer ε-caprolactone/1,5-dioxepan-2-one, 70:30 ratio.
**Figure S76.** Homo-probabilities vs. chain length of copolymer δ-valerolactone/1,5-dioxepan-2-one, 50:50 ratio.

![Graph](image1)

**Figure S77.** Homo-probabilities vs. chain length of copolymer ε-caprolactone/trimethylene carbonate.

![Graph](image2)

**Figure S78.** Homo-probabilities vs. chain length of copolymer lactide/1,5-dioxepan-2-one.
**Figure S79.** Homo-probabilities vs. chain length of copolymer ε-caprolactone/lactide.