Supporting Information for

In-Chain Poly(phosphonate)s via Acyclic Diene Metathesis Polycondensation

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Tables

Table S1. Synthetic results for in-chain poly(phosphonate)s prepared by ADMET polymerization in solution using 1-chloronaphthalene as solvent or in bulk.

<table>
<thead>
<tr>
<th>#</th>
<th>catalyst</th>
<th>Cat. / eq</th>
<th>V_{solvent}/mL</th>
<th>t / h</th>
<th>M_n /gmol(^{-1})</th>
<th>M_w/M_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(1)-a</td>
<td>Grubbs 1(^{st}) Gen.</td>
<td>0,06</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Poly(1)-b</td>
<td>Grubbs 2(^{nd}) Gen.</td>
<td>0,06</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Poly(2)-a</td>
<td>Grubbs 1(^{st}) Gen.</td>
<td>0,09</td>
<td>2</td>
<td>48</td>
<td>8700*</td>
<td>-</td>
</tr>
<tr>
<td>Poly(2)-b</td>
<td>Grubbs 1(^{st}) Gen.</td>
<td>0,06</td>
<td>2</td>
<td>48</td>
<td>8000*</td>
<td>-</td>
</tr>
<tr>
<td>Poly(3)-a</td>
<td>Grubbs 1(^{st}) Gen.</td>
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<td>2</td>
<td>48</td>
<td>27900</td>
<td>1.67</td>
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<tr>
<td>Poly(3)-b</td>
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<td>2</td>
<td>48</td>
<td>20600</td>
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<tr>
<td>Poly(3)-c</td>
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<td>24</td>
<td>5030</td>
<td>1.41</td>
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<tr>
<td>Poly(4)-a</td>
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<td>2</td>
<td>48</td>
<td>27600</td>
<td>1.68</td>
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<tr>
<td>Poly(4)-b</td>
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<td>2</td>
<td>48</td>
<td>6700</td>
<td>2.49</td>
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<td>0,03</td>
<td>-</td>
<td>24</td>
<td>3640</td>
<td>8.4</td>
</tr>
</tbody>
</table>

* determined by vapor pressure osmometry
$^1$H, $^{13}$C, $^{31}$P NMR spectra

Monomer Spectra:

Figure S1. $^1$H NMR of compound 1 at 500 MHz in CDCl$_3$ at 298 K.
Figure S2. $^{13}$C NMR of compound 1 at 126 MHz in CDCl$_3$ at 298 K.

Figure S3. $^{31}$P NMR of compound 1 at 202 MHz in CDCl$_3$ at 298 K.
Figure S4. $^1$H NMR of compound 2 at 500 MHz in CDCl$_3$ at 298 K.

Figure S5. $^{13}$CNMR of compound 2 at 176 MHz in CDCl$_3$ at 298 K.
**Figure S6.** $^{31}$P NMR of compound 2 at 283 MHz in CDCl$_3$ at 298 K.

**Figure S7.** $^1$H NMR of compound 4 at 700 MHz in CDCl$_3$ at 298 K.
Figure S8. $^{31}$P NMR of compound 4 at 283 MHz in CDCl$_3$ at 298 K.

Figure S9. $^1$H NMR of compound 3 at 700 MHz in CDCl$_3$. 
Figure S10. $^{13}$C NMR of compound 3 at 176 MHz in CDCl$_3$ at 298 K.

Figure S11. $^{31}$P NMR of compound 3 at 283 MHz in CDCl$_3$ at 298 K.
Figure S12. $^1$H NMR of compound 5 at 300 MHz in CDCl$_3$. 
Polymer NMR Spectra

The monomer architecture allows three different types of conjunction, i.e. head to tail, tail to tail and head to head (see Scheme S1), all contained in the obtained polymers. In the following, the polymer structures are presented in the simplified head to tail structure.

Scheme S1. Possible conjunctions within the polymer structure.

Figure S13. $^1$H NMR of poly(3) at 500 MHz in CDCl$_3$. 
Figure S14. $^{13}$C NMR of poly(3) at 126 MHz in CDCl$_3$ at 298 K.

Figure S15. $^{31}$P NMR of poly(3) at 202 MHz in CDCl$_3$. 
Figure S16. $^1$H NMR of poly(3)-H at 500 MHz in CD$_2$Cl$_2$

Figure S17. $^{13}$C NMR of poly(3)-H at 126 MHz in CD$_2$Cl$_2$ at 298 K.
Figure S18. $^{31}$P NMR of poly(3)-H at 202 MHz in CD$_2$Cl$_2$.

**Size exclusion chromatography**

![Size exclusion chromatography graph](image)
**Figure S19.** SEC elugrams of poly(3)s prepared ADMET polymerization.

**Figure S20.** SEC elugrams of poly(4)s prepared ADMET polymerization.

**Figure S21.** SEC elugrams of poly(5) prepared ADMET polymerization.
**DSC, TGA**

**Figure S22.** TGA thermogram of poly(4)-a and the corresponding hydrogenated polymer poly(4)-H.

**Figure S23.** DSC thermogram of Poly(2)-a and the corresponding hydrogenated polymer Poly(2)-H.
Figure S24. DSC thermogram of Poly(4)-a and the corresponding hydrogenated polymer Poly(4)-H.
Figure S25. DSC thermogram (heating curve) of poly(5)-H.

Figure S26. EELS thickness measurements for solution grown crystals of poly(3)-H.
Long period: 2.4 nm

Figure S27. SAXS measurements of poly(3)-H.

Figure S28. TEM BF micrograph of solution grown crystals of poly(3)-H from n-octane solution.

Additional References
