Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Polycycloacetals via Polytransacetalization of Diglycerol Bisacetonide

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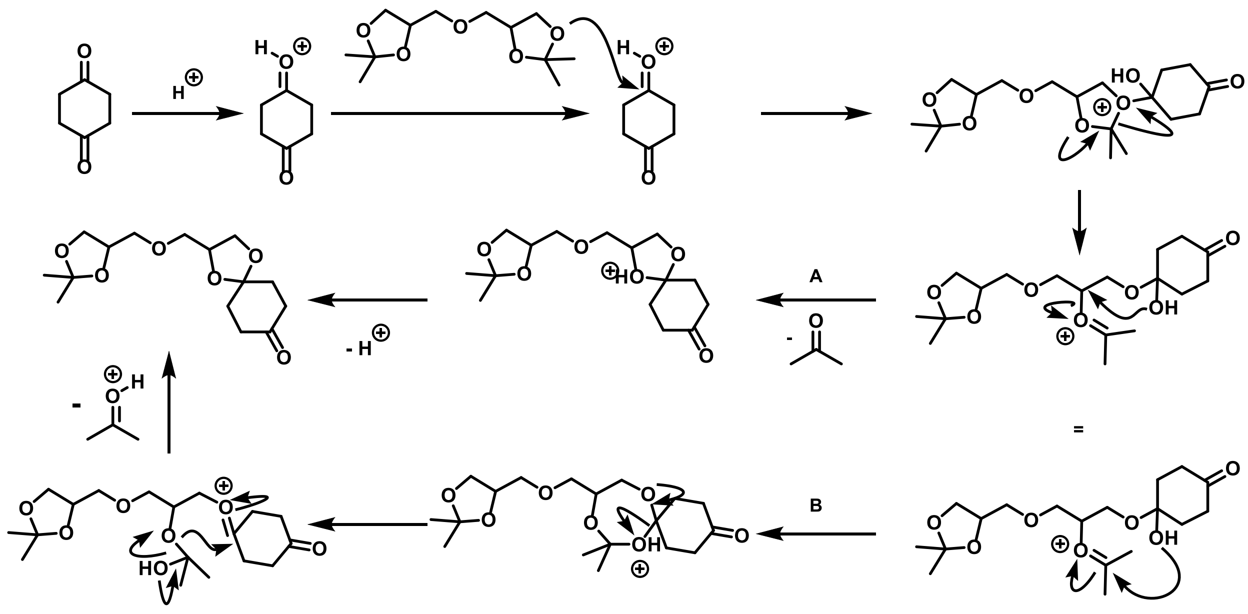

Scheme S1. Representation of postulated detailed mechanisms (A and B).[1]

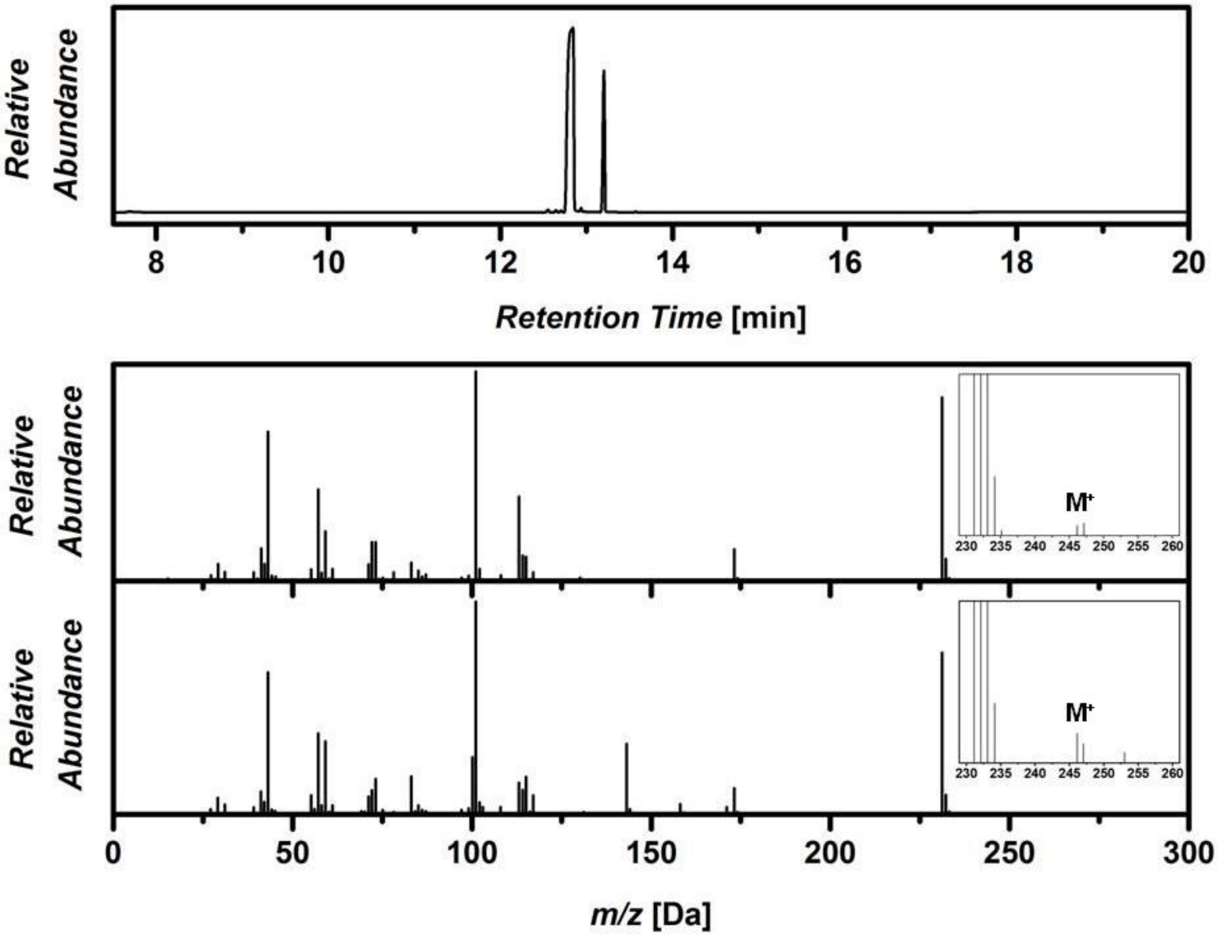

Figure S1. GC-MS data of DGA, including elugram (top), and mass spectra corresponding to the signal at 12.84 min (middle) and the signal at 13.20 min (bottom) with inserts showing an enlargement of the range in m/z from 230-260 Da.

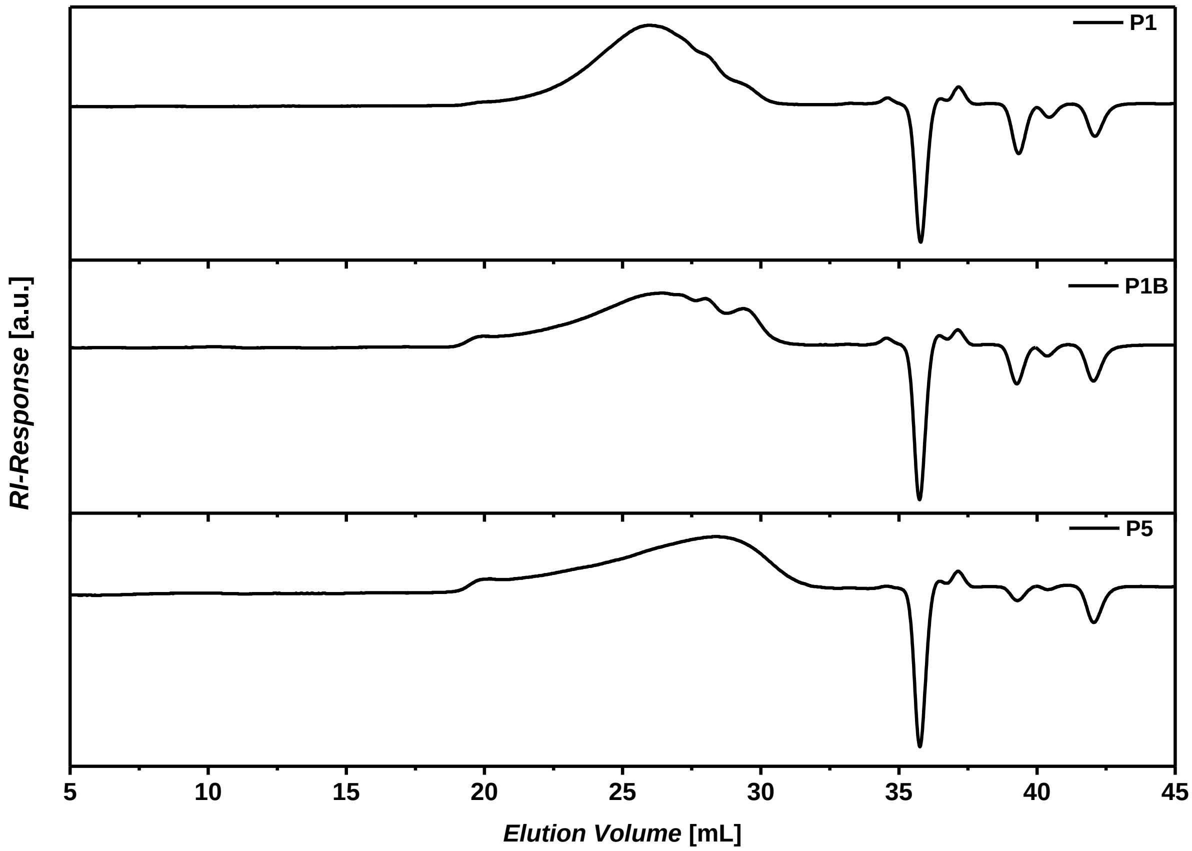

Figure S2. SEC traces of the polycycloacetals **P1**, **P1B** and **P5** in $CHCl_3$. The shoulders visible at low elution volumina in the SEC traces of **P1B** and **P5** are due to the exclusion volume of the column.

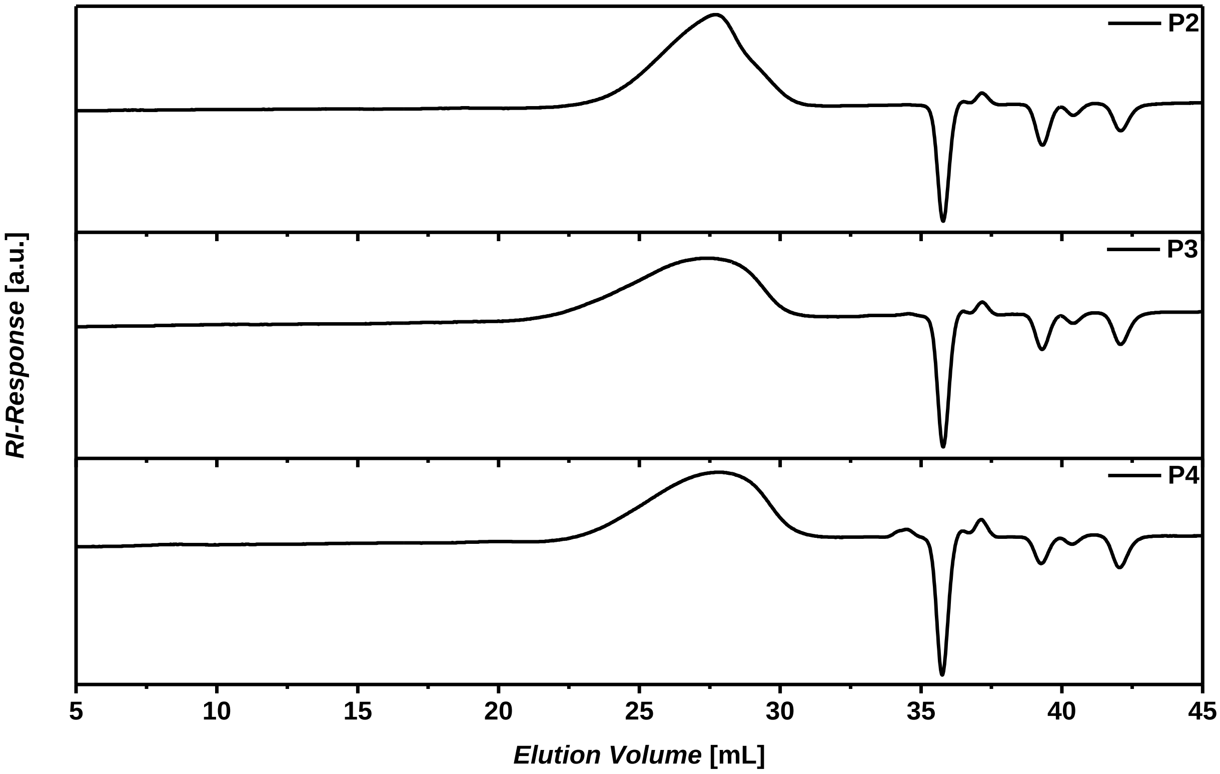

Figure S3. SEC traces of the copolycycloacetals **P2-4** in $CHCl_3$.

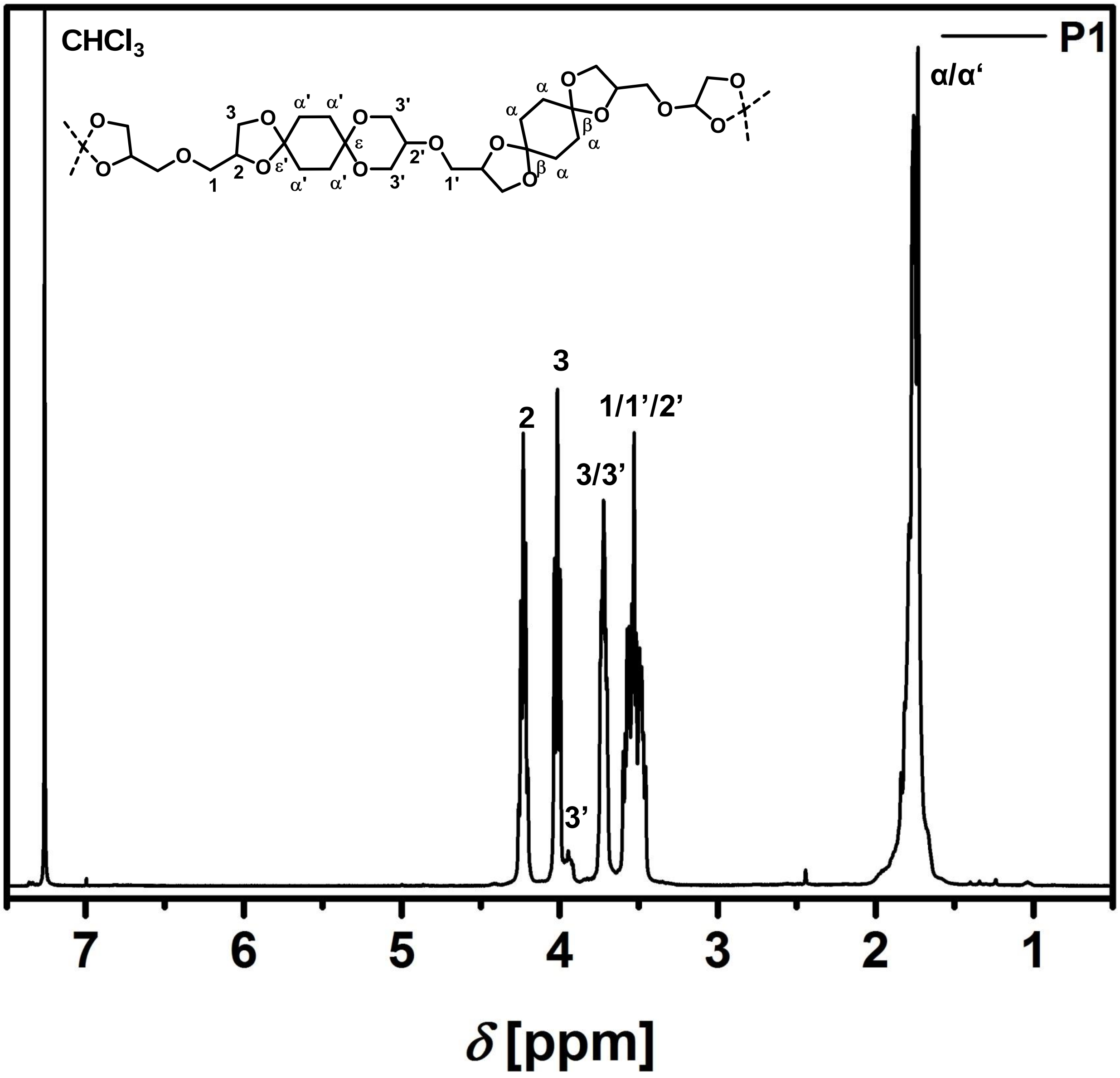

Figure S4. ^{1}H-NMR spectrum of **P1** in CDCl$_3$.

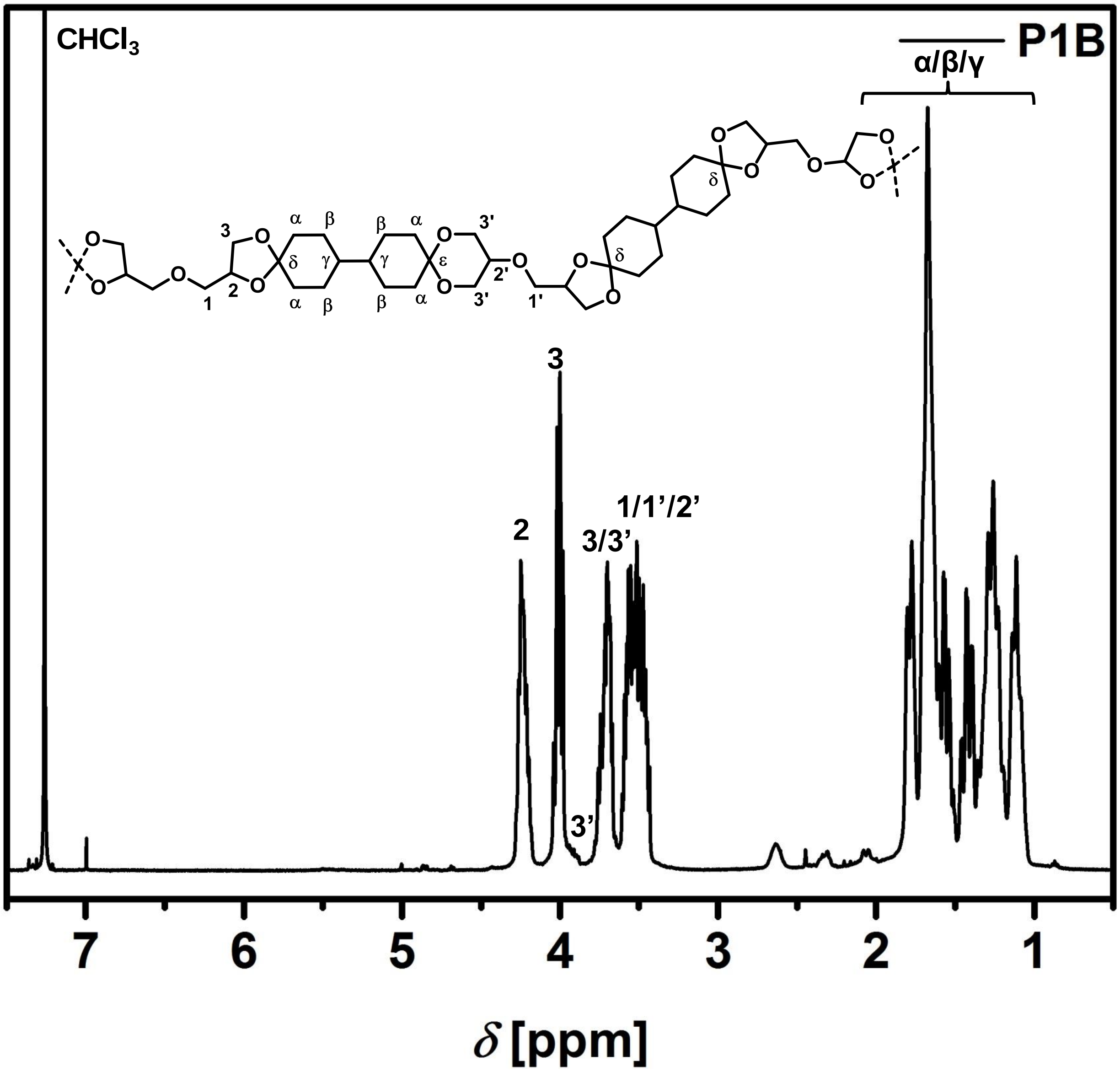

Figure S5. ^{1}H-NMR spectrum of **P1B** in $CDCl_3$.

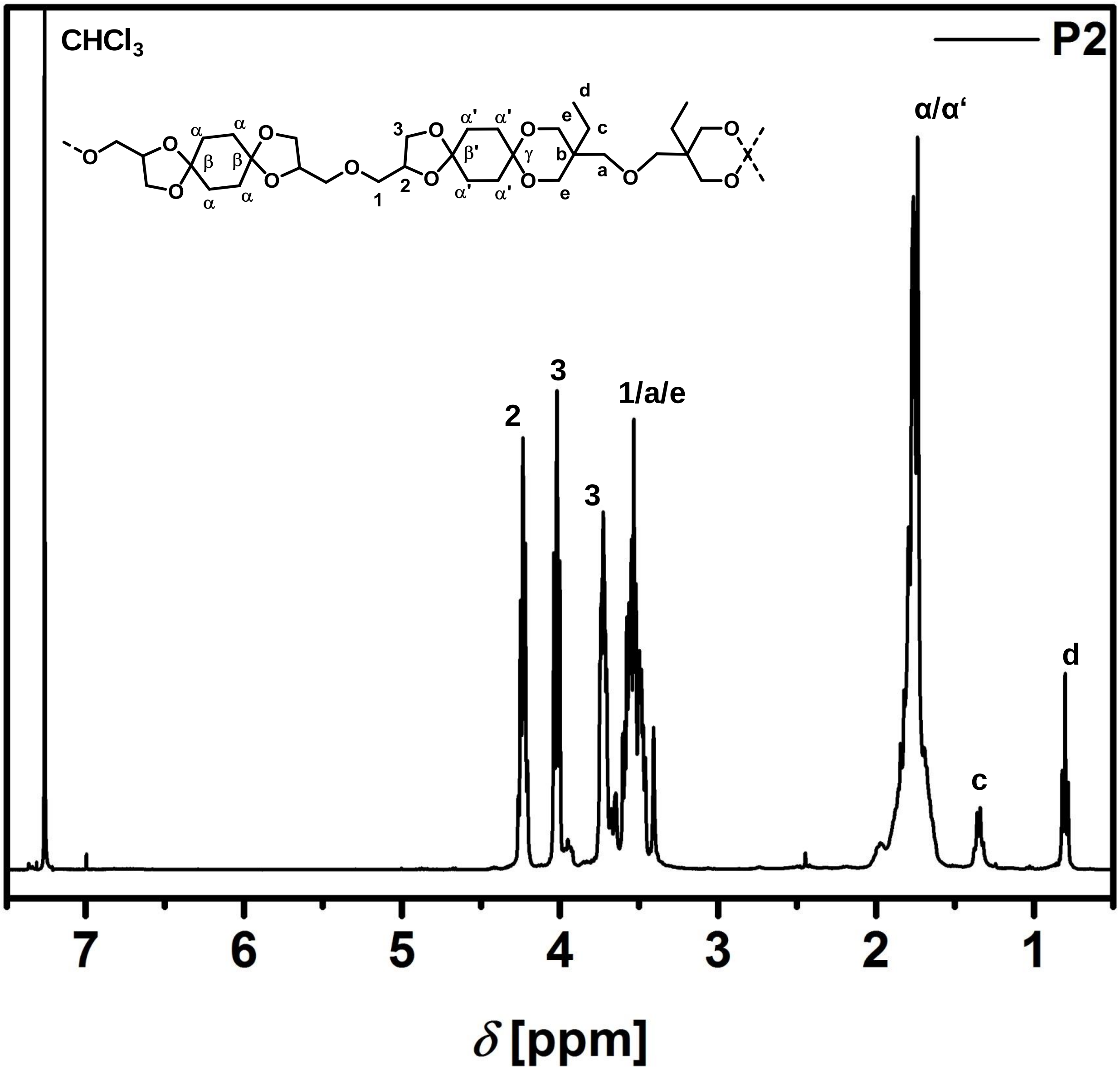

Figure S6. ^{1}H-NMR spectrum of **P2** in $CDCl_3$. The resonances of the repeat unit formed by reaction with the regioisomer DGA are also visible but were not assigned for simplicity (compare Figure S4).

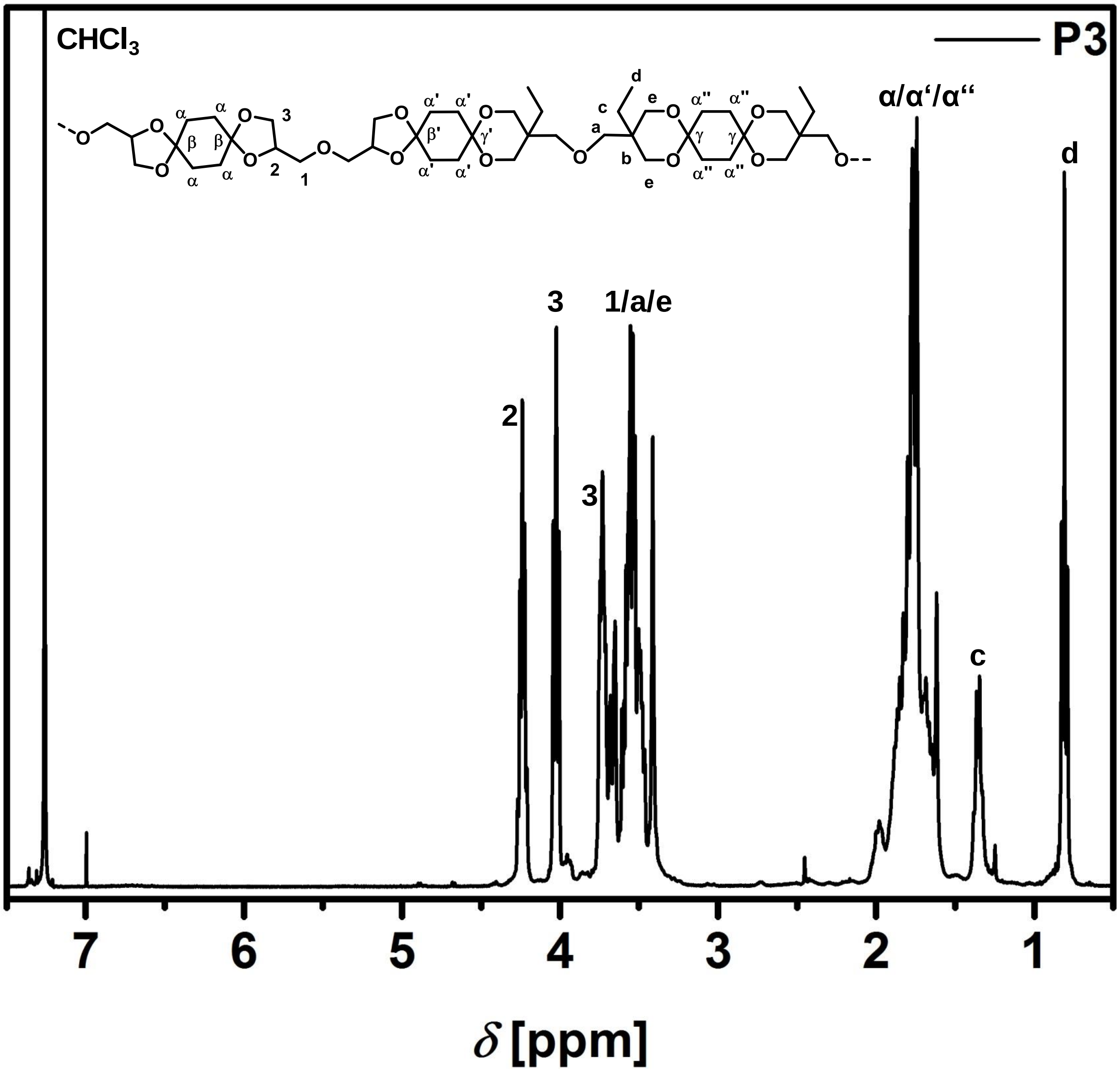

Figure S7. ^{1}H-NMR spectrum of **P3** in CDCl$_3$. The resonances of the repeat unit formed by reaction with the regioisomer DGA are also visible but were not assigned for simplicity (compare Figure S4).

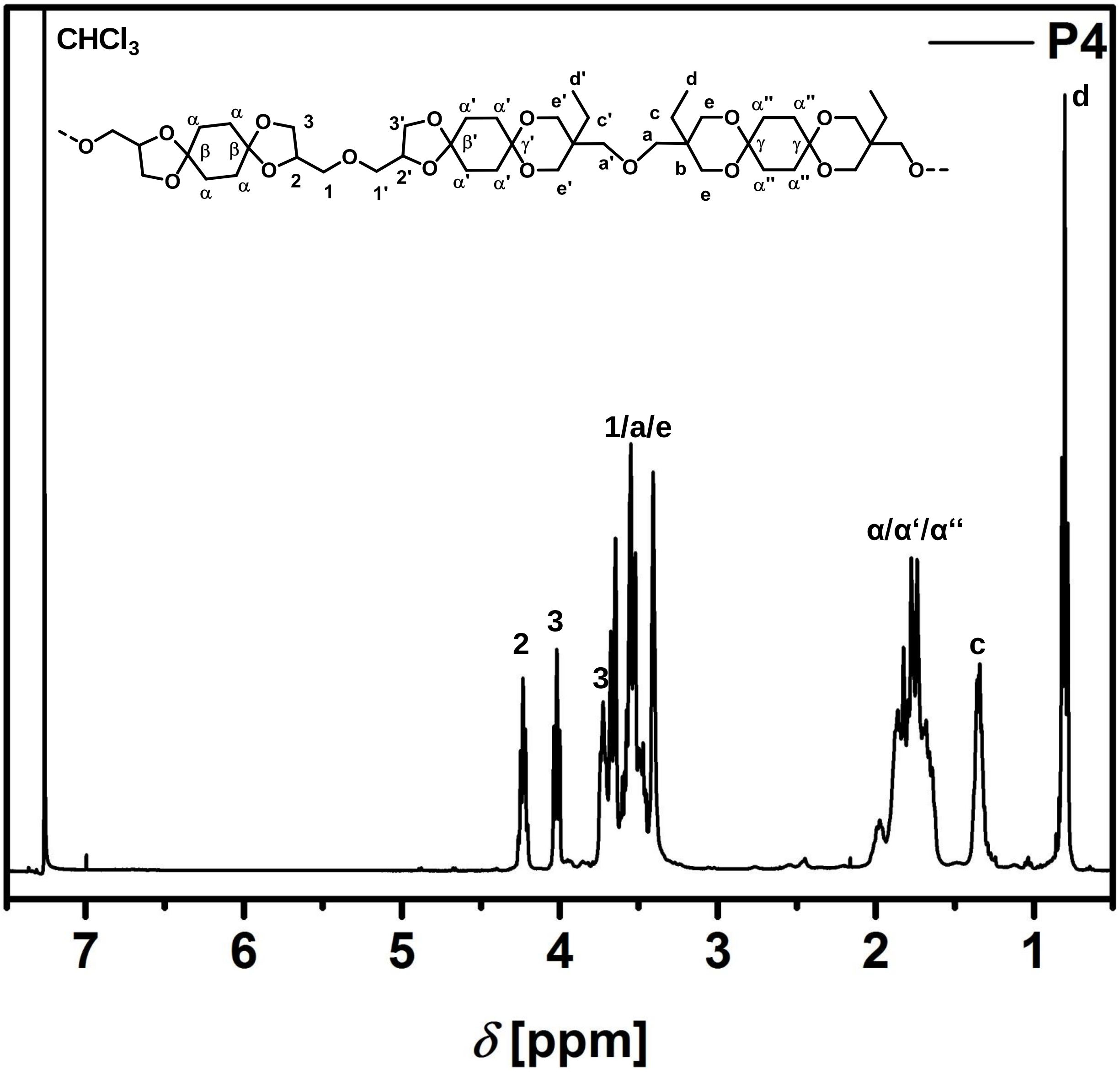

Figure S8. ^{1}H-NMR spectrum of **P4** in CDCl$_3$. The resonances of the repeat unit formed by reaction with the regioisomer DGA are also visible but were not assigned for simplicity (compare Figure S4).

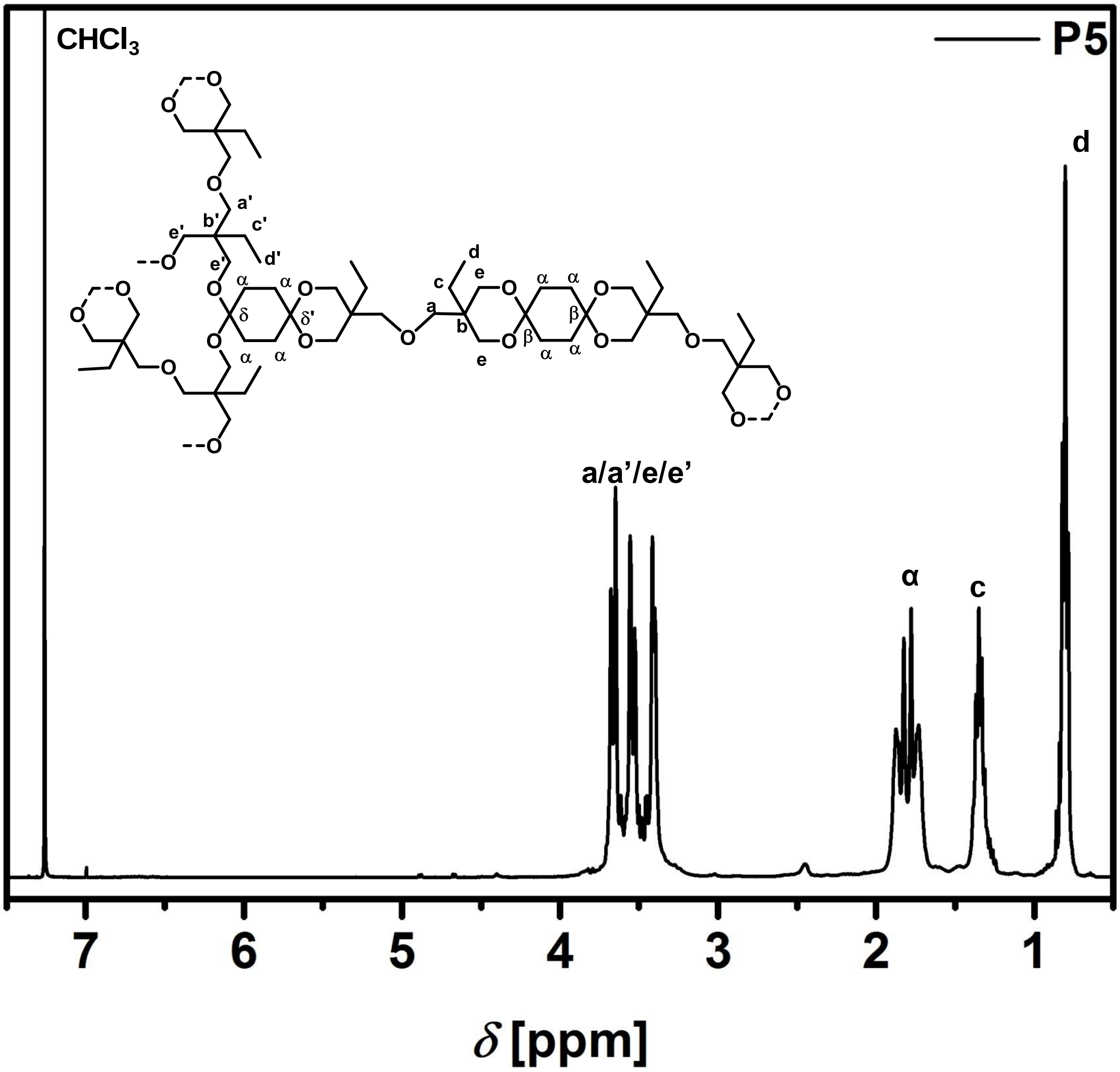

Figure S9. ^{1}H-NMR spectrum of **P5** in CDCl$_3$.

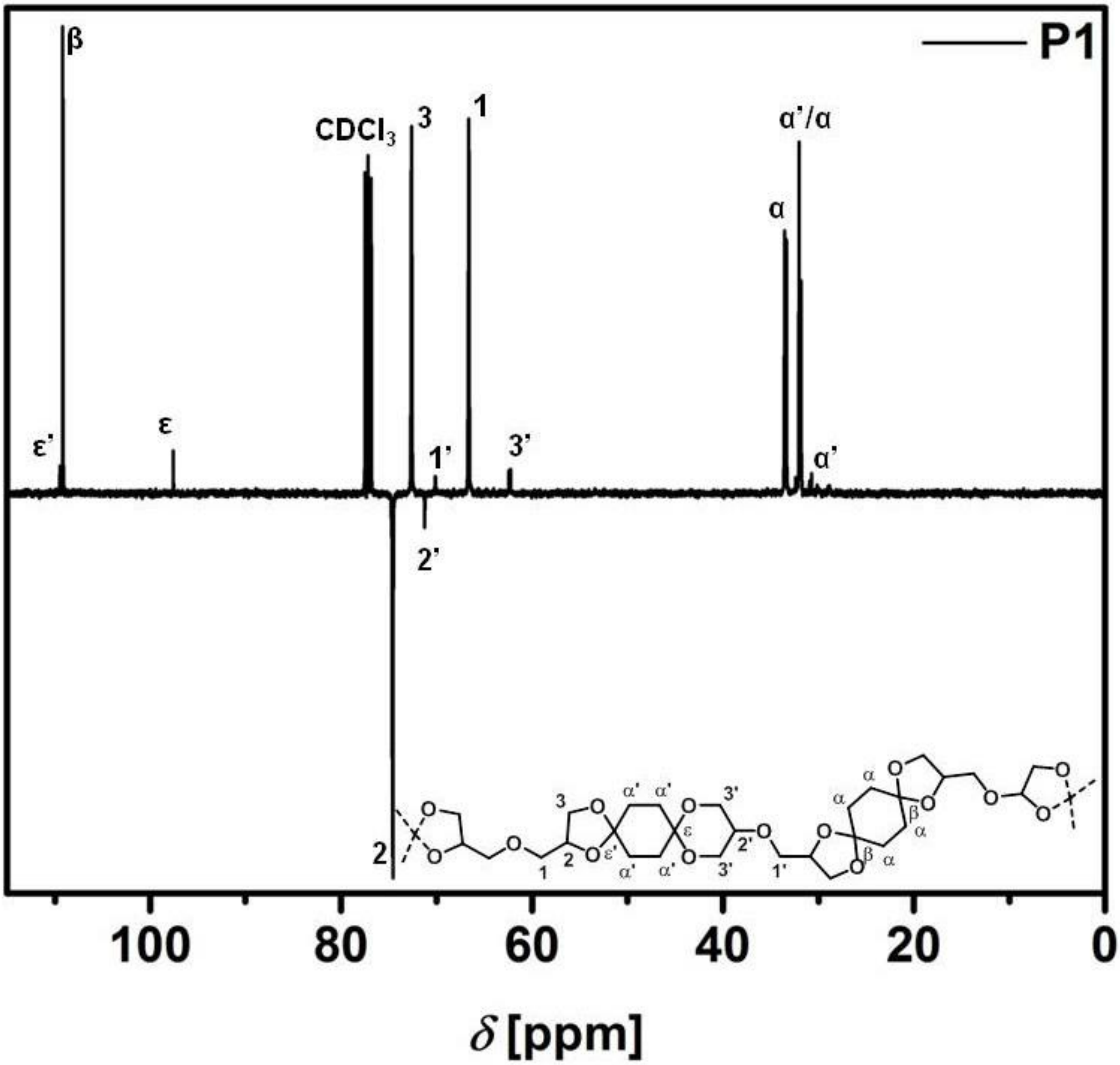

Figure S10. ^{13}C-NMR spectrum of **P1** in $CDCl_3$.

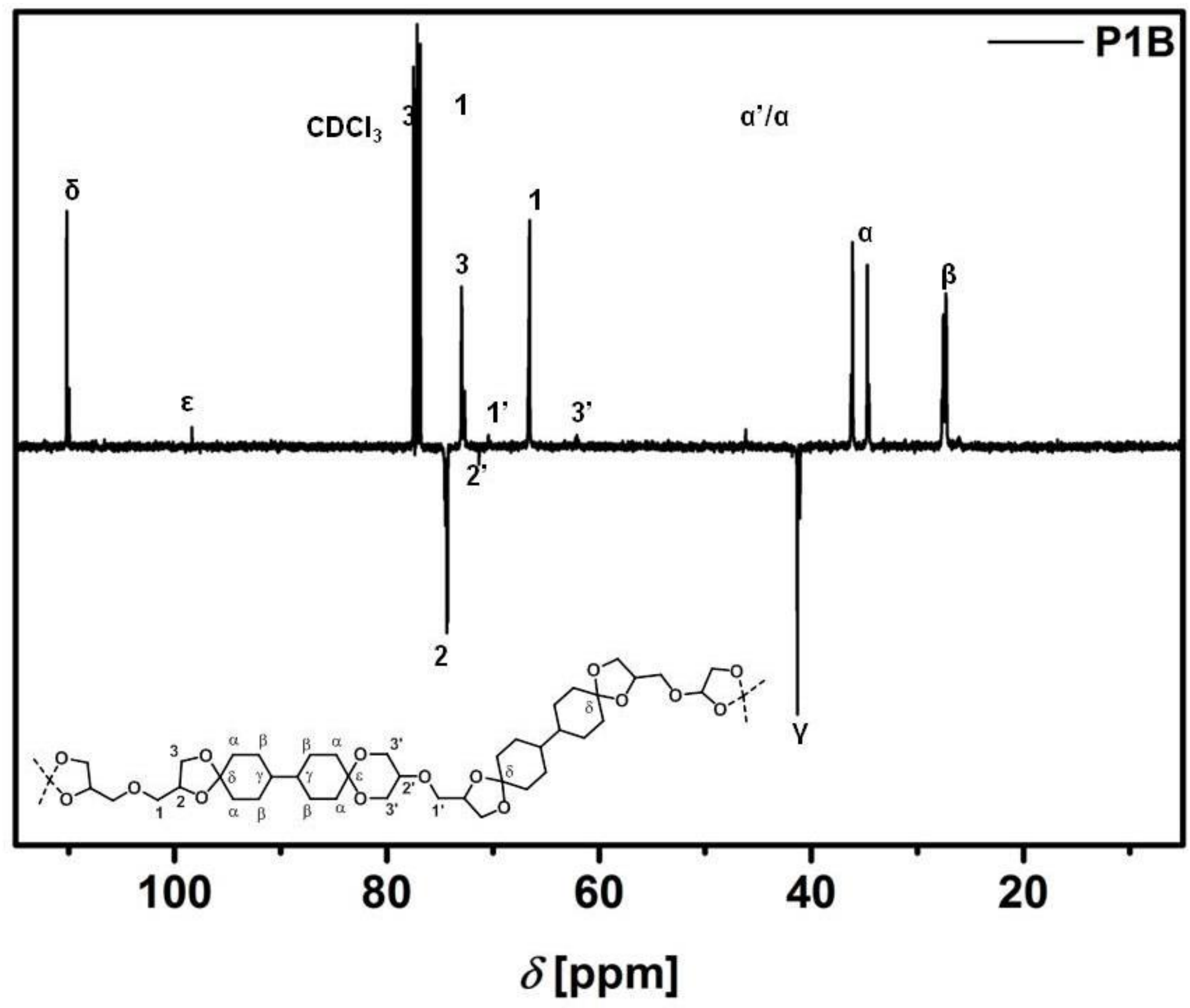

Figure S11. ^{13}C-NMR spectrum of **P1B** in CDCl$_3$.

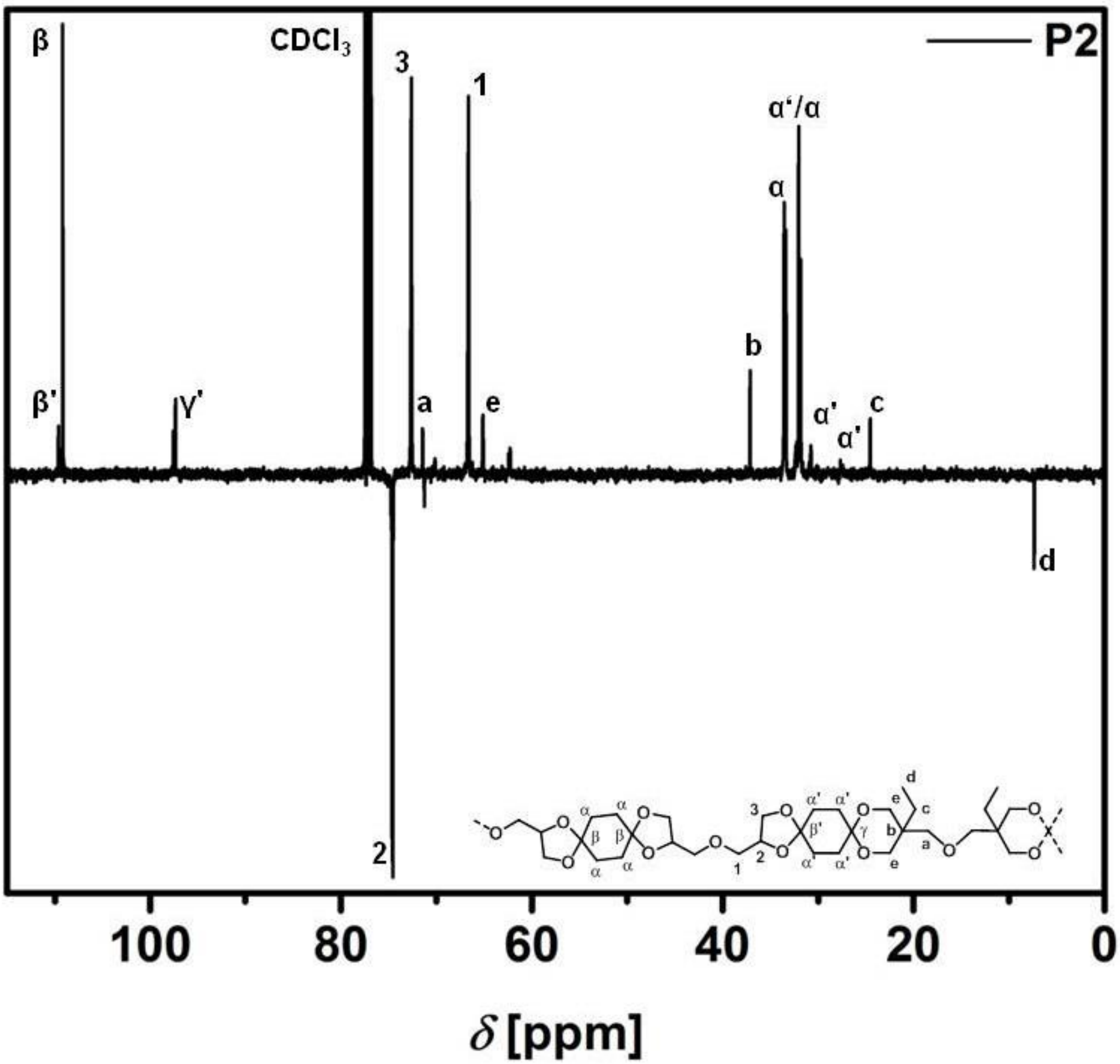

Figure S12. ^{13}C-NMR spectrum of **P2** in CDCl$_3$. The resonances of the repeat unit formed by reaction with the regioisomer DGA are also visible but were not assigned for simplicity (compare Figure S10).

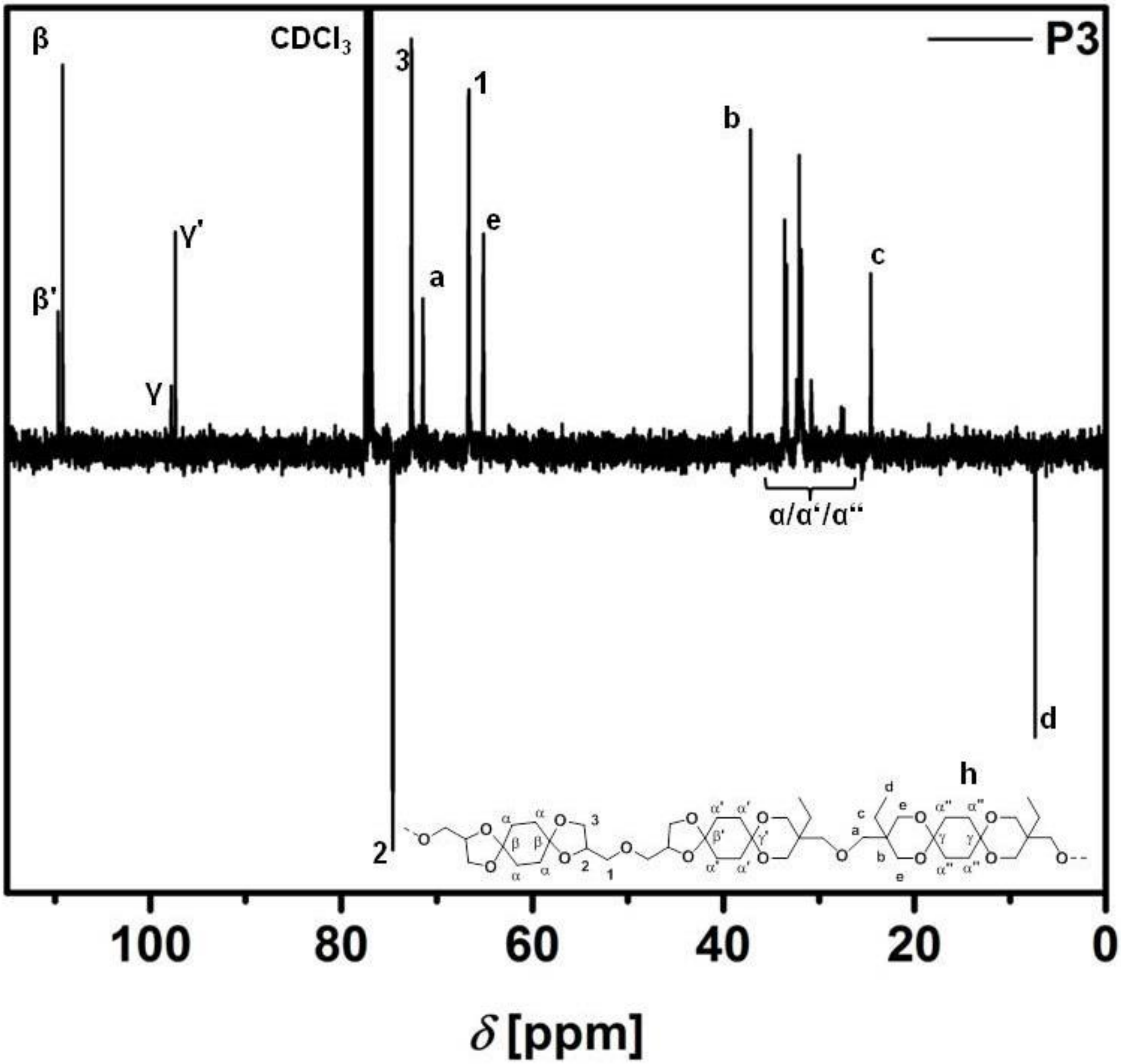

Figure S13. ^{13}C-NMR spectrum of **P3** in CDCl$_3$.

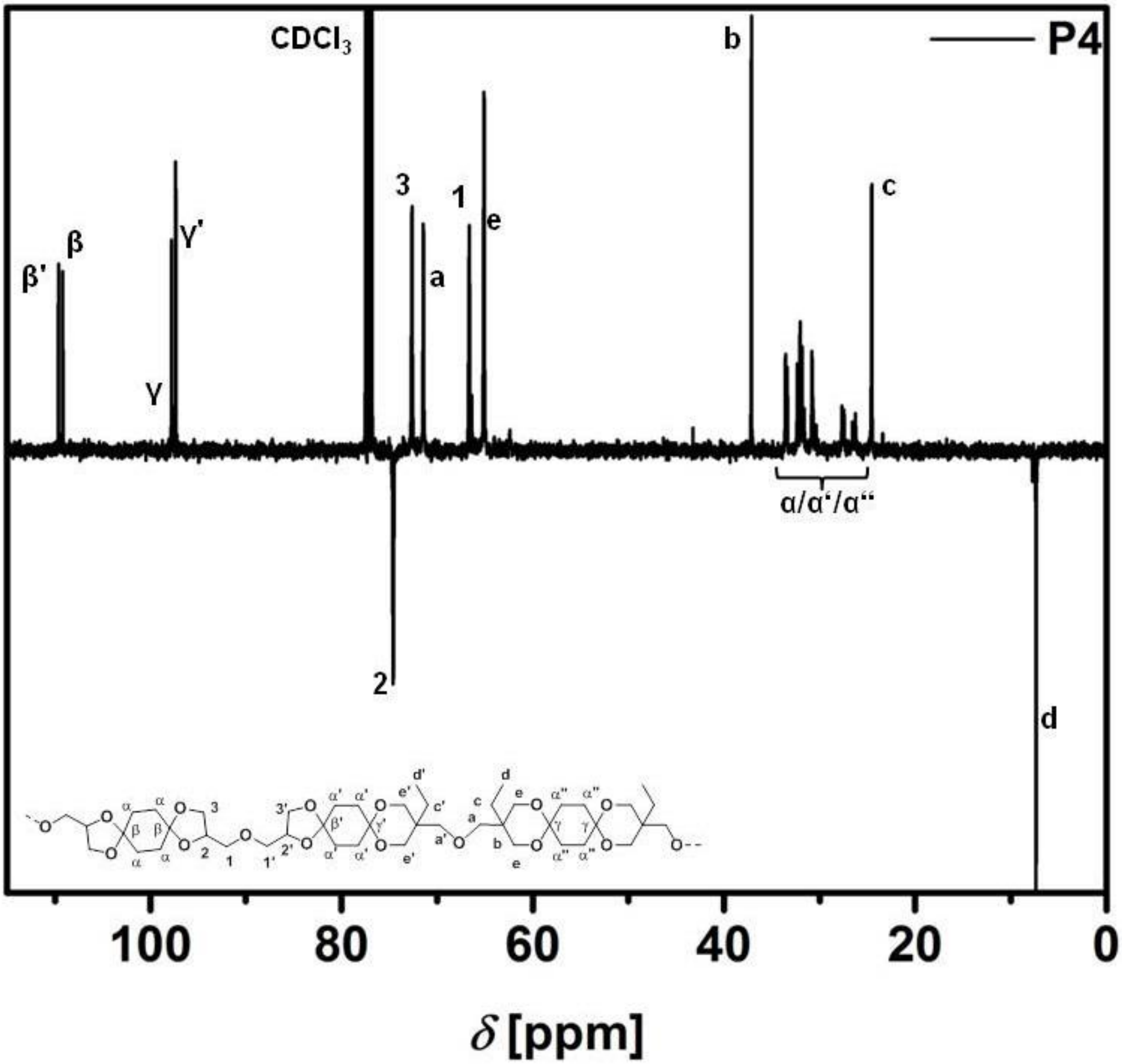

Figure S14. ^{13}C-NMR spectrum of **P4** in CDCl$_3$.

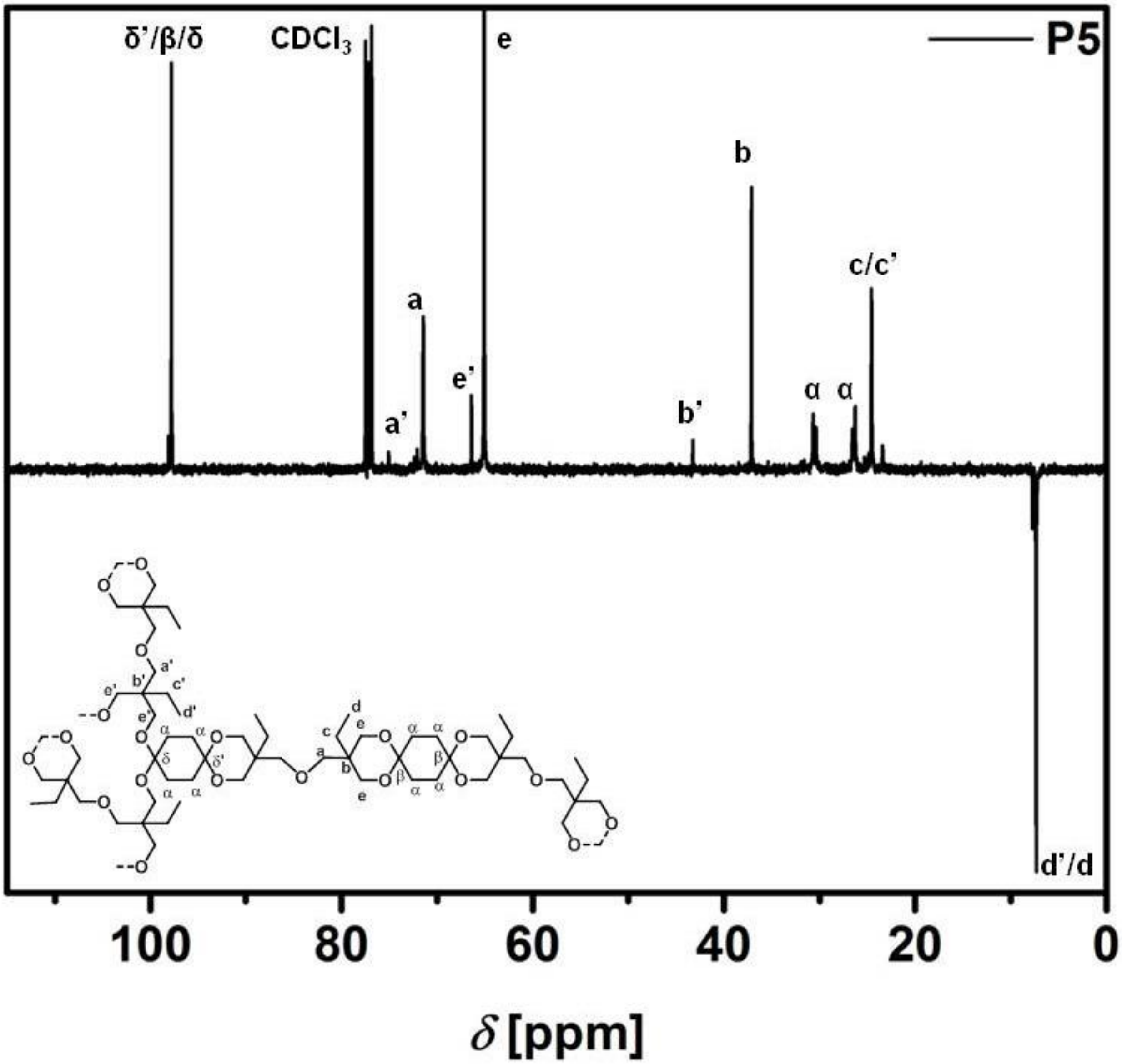

Figure S15. ^{13}C-NMR spectrum of **P5** in CDCl$_3$.

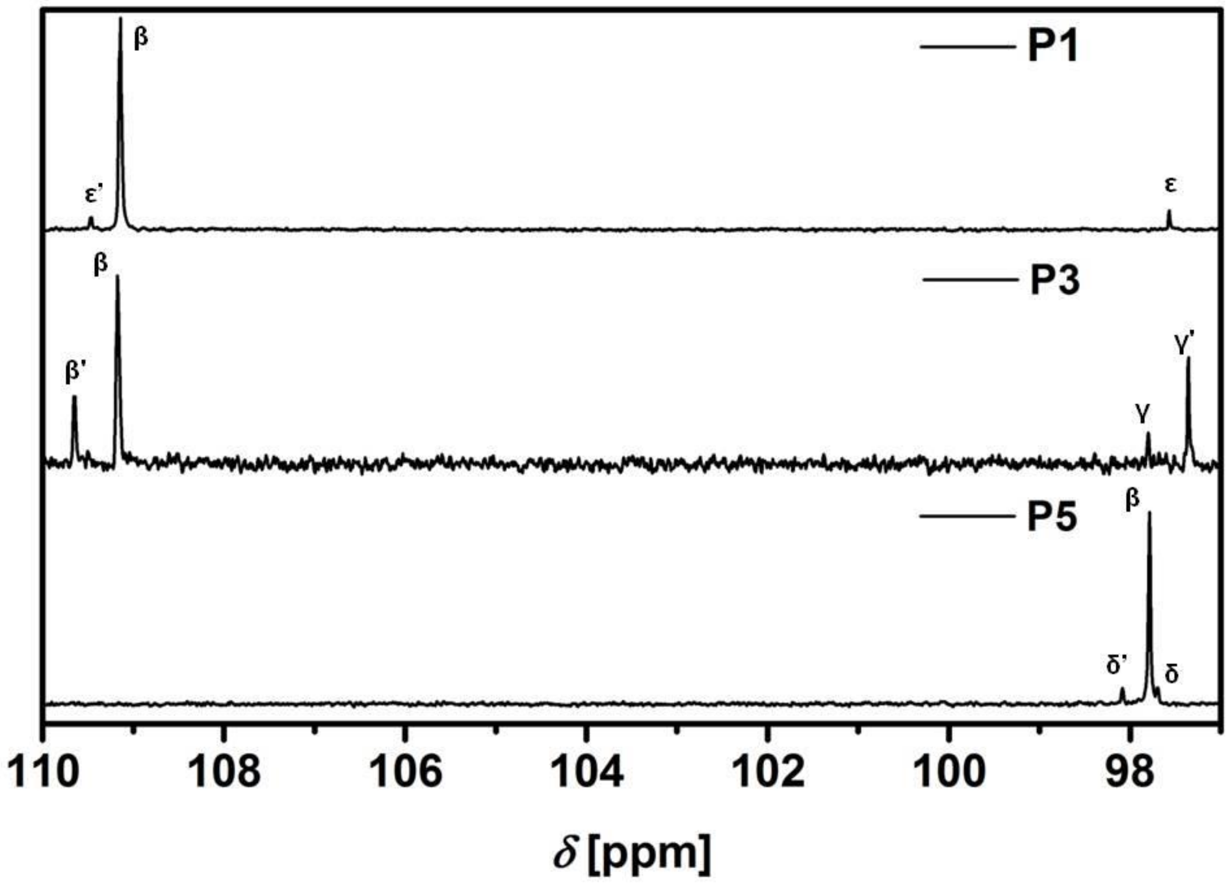

Figure S16. Comparison of the ^{13}C-NMR spectra of **P10**, **P13** and **P5** showing the resonances of the different acetal bonds. For annotation see Figures S4, S6, and S15.

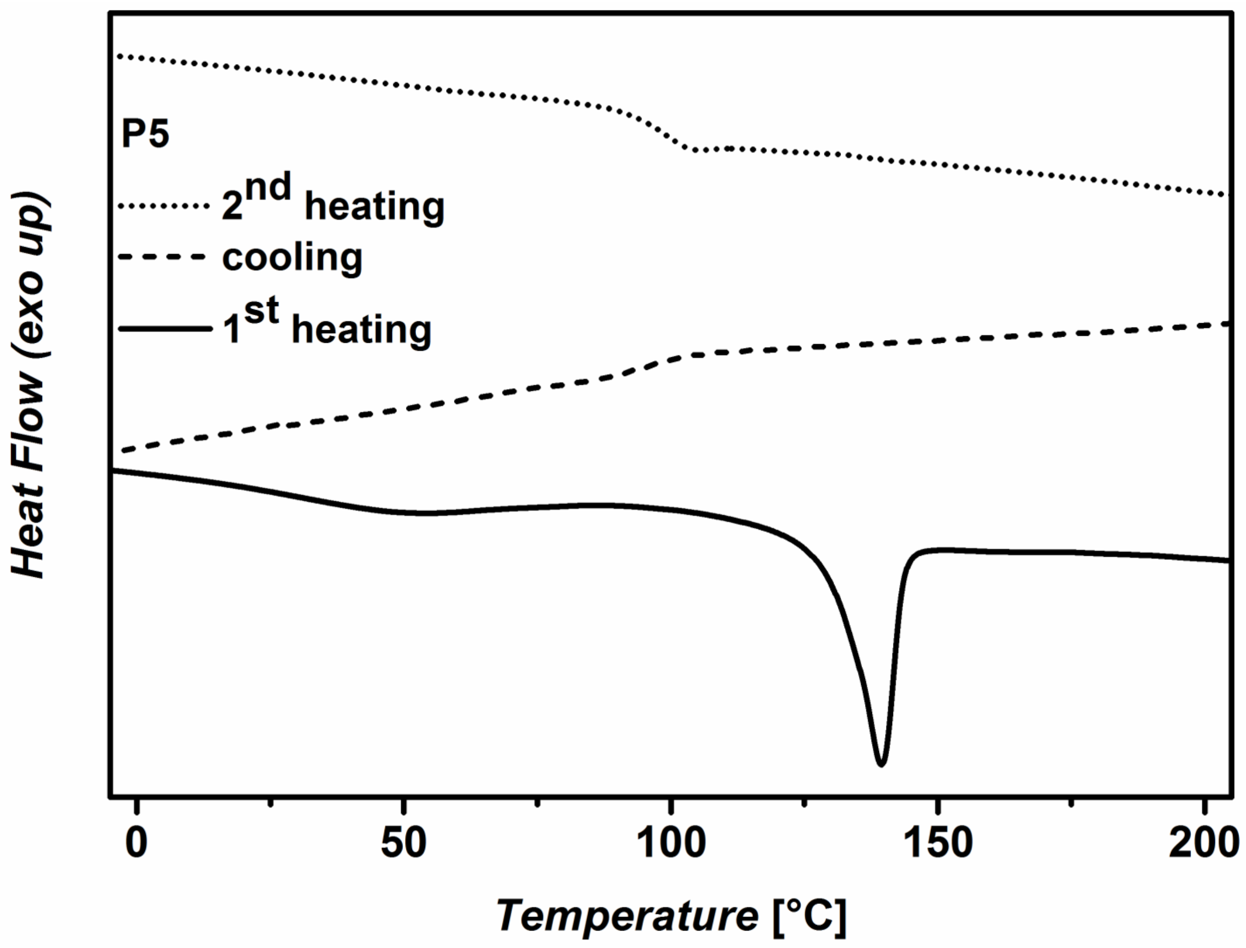

Figure S17. DSC data of **P5** including the first heating and the first cooling scan. A melting peak is only detected in the first heating scan.

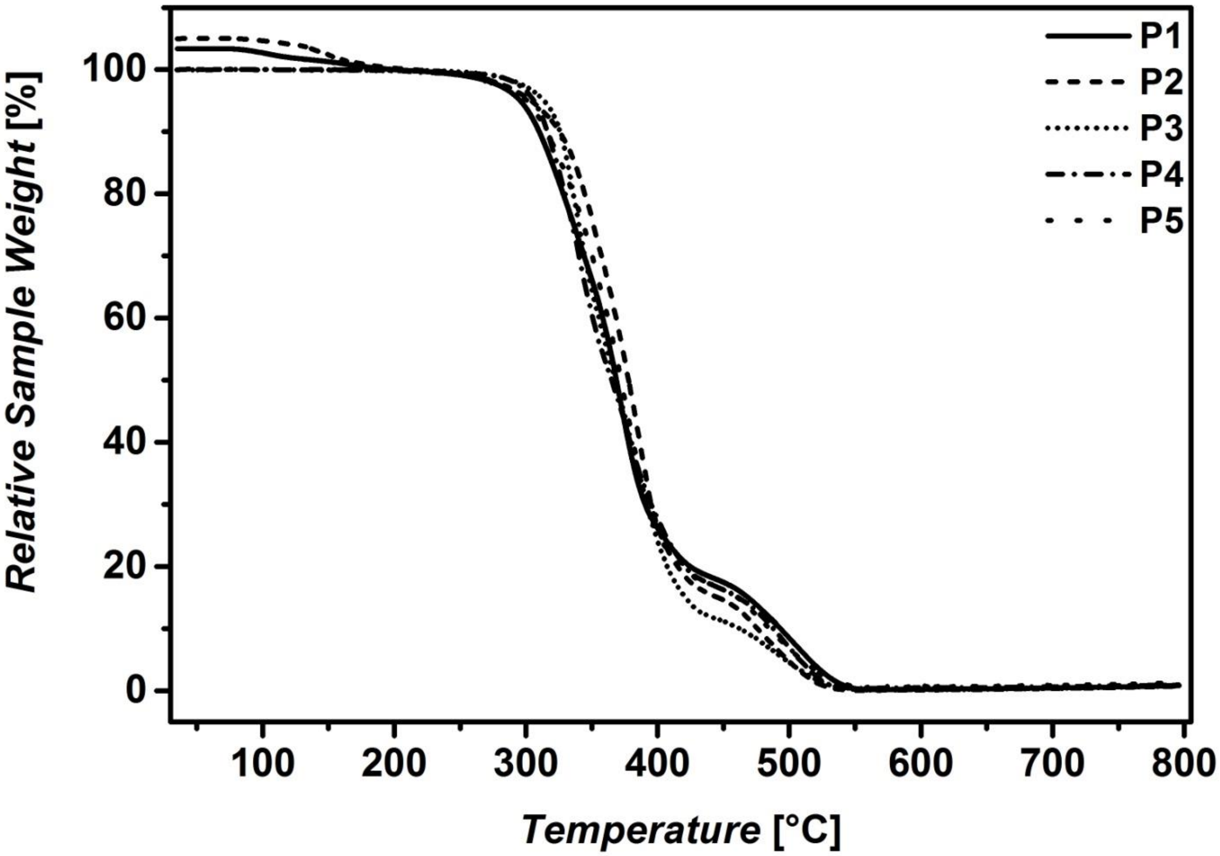

Figure S18. TGA traces of polymers **P1-5** measured under air. No significant weight loss is detected at temperatures below 300 °C. The weight loss of approximately 5%, which occurs for samples P3 and P4 at 100-150 °C, is due to solvent residues and the traces were corrected accordingly.

Table S1. Processing parameters for compression molding and SEC data after processing for **P1-5**.

	$T_{\mathrm{oven}}/T_{\mathrm{press}}$ [°C]	P [t]	$M_{\mathrm{n,\ processed}}$ [kg mol^{-1}]	$Đ_{\mathrm{processed}}$
P1	190/175	1.5	32.2	3.6
	-/225	0.5	4.6	3.4
P1B	-/215	0.5	2.6	4.6
P2	190/165	1.5	25.2	4.3
P3	145/135	1.5	23.2	2.7
P4	155/145	1.5	18.0	1.9
P5	190/165	1.5	19.7	5.2

REFERENCES

1. Moraes, L. A. B.; Mendes, M. A.; Sparrapan, R.; Eberlin, M. N. Transacetalization with gaseous carboxonium and carbosulfonium ions. *J. Am. Soc. Mass. Spectrom.* **2001,** *12*, 14-22.