# Water-Soluble "Poly(propylene oxide)" by Random Copolymerization of Propylene Oxide with a Protected Glycidol Monomer

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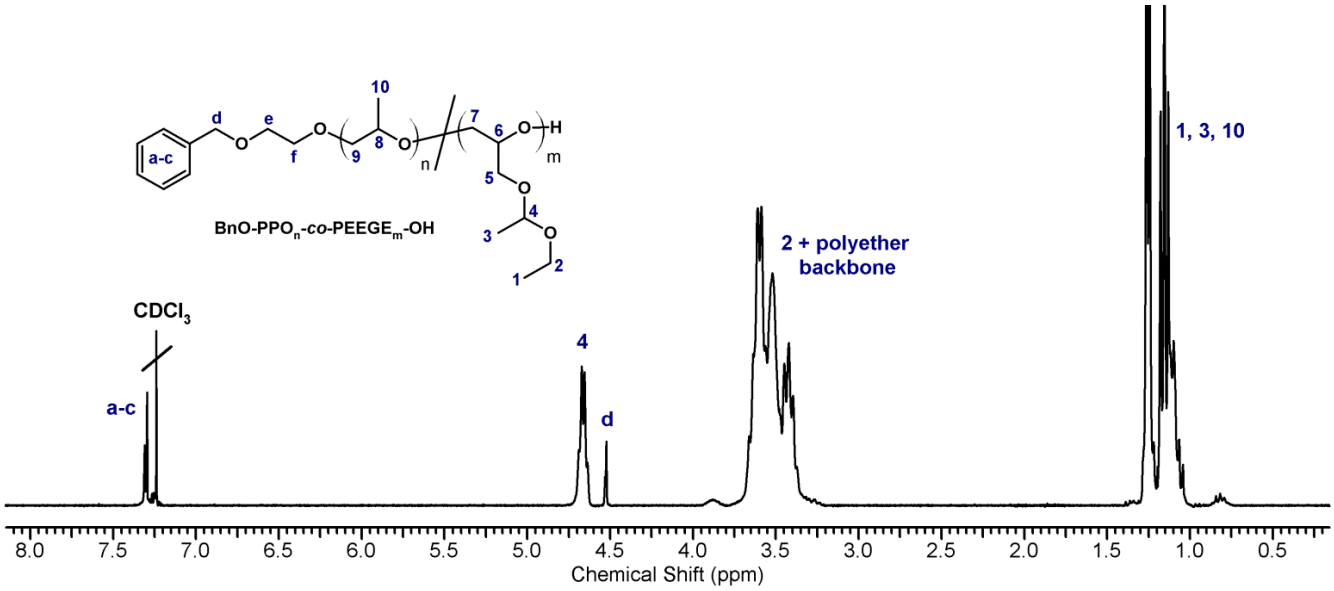


**Figure S1.** $^1$H NMR spectrum and structural assignments of BnO-PPO$_{20}$-*co*-PEEGE$_{30}$-OH.

$^1$H NMR analysis permits the calculation of the ratio of comonomers incorporated by determination of the fraction of EEGE units from the intensity of the acetal proton signal (**Figure S1**) when the initiator signal d is set to the value 2. After determination of the EEGE

content, the fraction of PO units can be calculated from the signals of the methyl groups 1, 3 and 10 by subtraction of the EEGE fraction from the overall signal intensity.

$$\#EEGE = I_{Acetal}$$

$$\#PO = \frac{I_{Methyl} - 6 \times I_{Acetal}}{3}$$

$$DP_n = \#EEGE + \#PO$$

$$\%EEGE = \frac{\#EEGE}{DP_n}$$

The overall degree of polymerization ($DP_n$) is the sum of both comonomers, and the EEGE content is calculated by dividing the number of EEGE units by the $DP_n$. All values are rounded to integer.

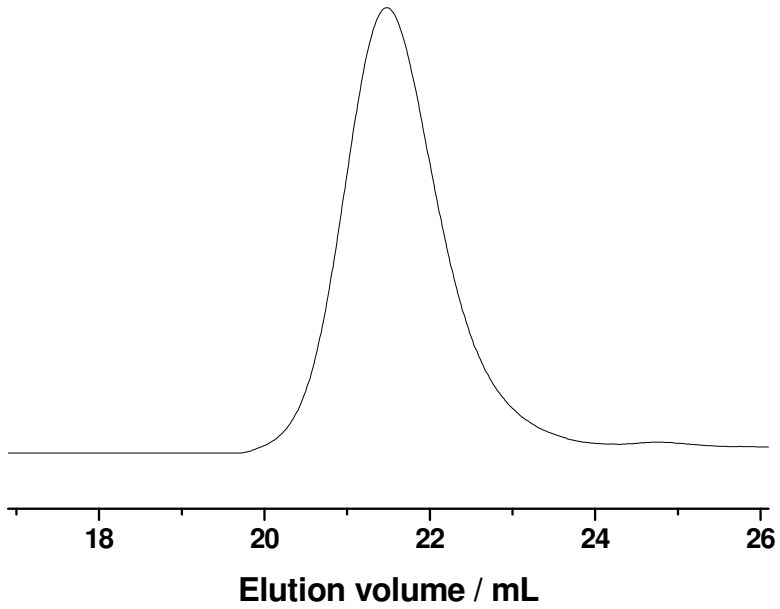


**Figure S2.** Example of a SEC curve of a BnO-$PPO_n$-*co*-$PEEGE_m$-OH copolymer polymerized in the NMR tube.

The molecular weight distributions of all samples obtained in the NMR experiments were narrow with polydispersities around 1.07. Plotting the polymer molecular weight versus total monomer conversion resulted in a linear graph in all cases (Fig. S3).

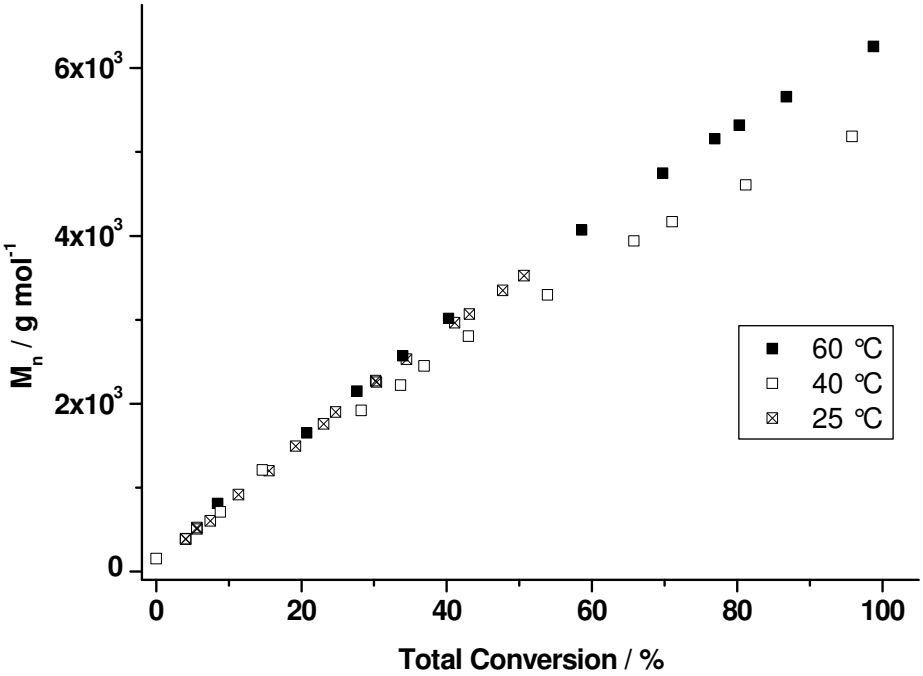


**Figure S3.** Molecular weight versus total conversion for copolymerization of propylene oxide with ethoxy ethyl glycidyl ether (15%) at 25, 40, and 60 °C measured in DMSO-$d_6$.

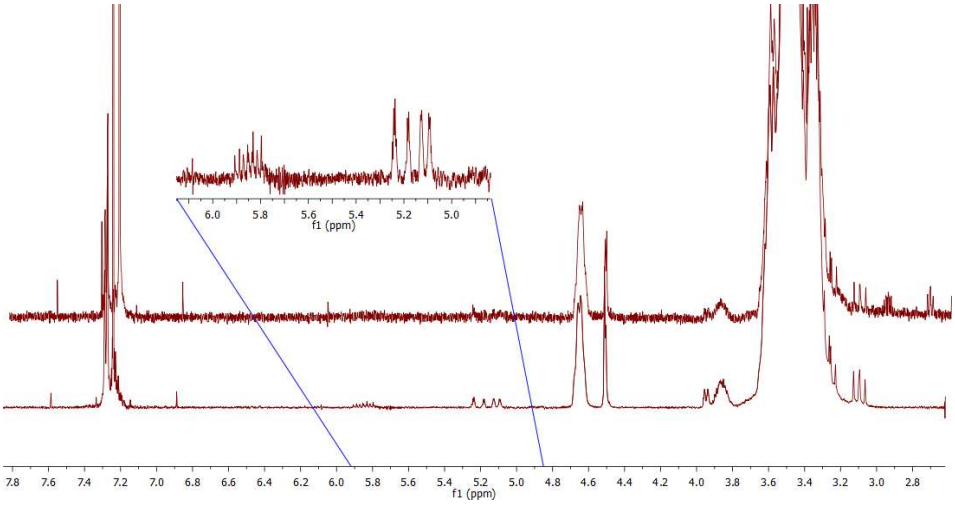


**Figure S4.** $^{1}$H NMR spectra of two BnO-PPO$_n$-*co*-PEEGE$_m$-OH copolymers, polymerized at 40 °C (a) and 60 °C (b).

Proton abstraction from propylene oxide and the subsequent rearrangement to an allyloxy anion would lead to polymer chains with a single hydroxyl end group and an allyl end group. The $^{1}$H NMR spectra of two BnO-PPO$_n$-*co*-PEEGE$_m$-OH copolymers, polymerized at 40 °C (a) and 60 °C (b), show complete suppression of allyloxy-initiated polymer chains.

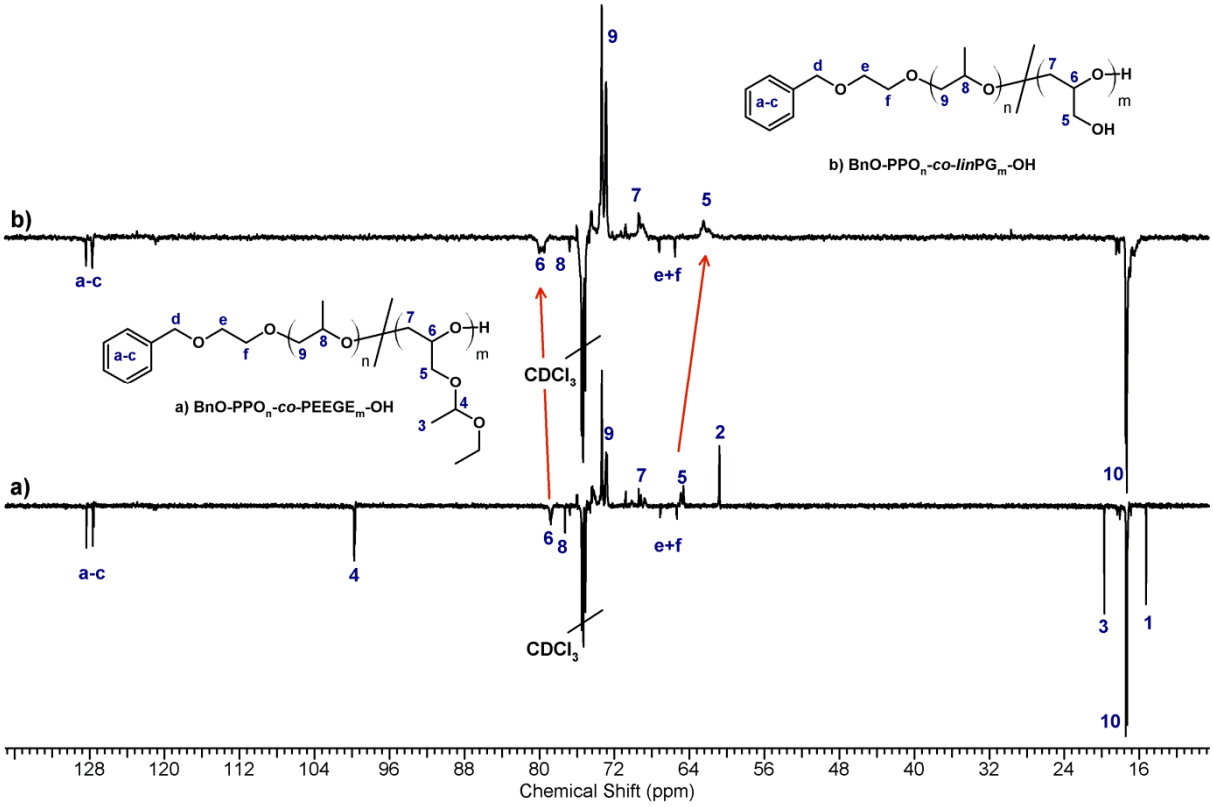


**Figure S5.** $^{13}$C NMR spectra (400 MHz, DMSO-$d_6$, DEPT) showing the cleavage of the acetal protecting groups: a) BnO-PPO$_n$-*co*-PEEGE$_m$-OH, b) BnO-PPO$_n$-*co*-*lin*PG$_m$-OH.

The cleavage of the acetal group upon acidic deprotection can also be monitored by $^{13}$C NMR spectroscopy. Full deprotection was confirmed by the disappearance of signals 1-4 of the ethoxy ethyl group and the shift of the remaining the methylene (5) and methine (6) carbon of the glycidol unit in the polymer chain.

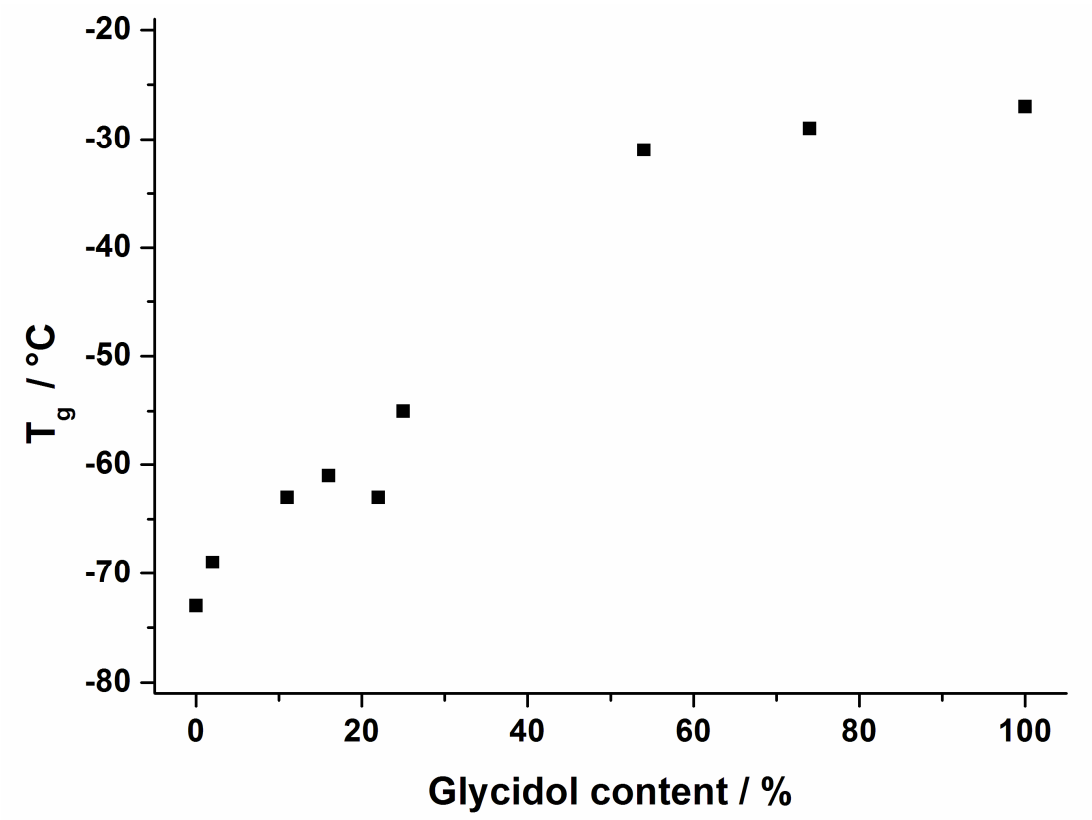


**Figure S6.** Correlation of the glass transition temperature ($T_g$) with glycidol content for the BnO-PPO$_n$-*co*-*lin*PG$_m$-OH copolymers.

Whereas the glass transition temperature ($T_g$) of the copolymers PPO-*co*-PEEGE shows only slight variation due to the very similar $T_g$s of the corresponding homopolymers, the glass transition temperature increases from -69 °C for BnO-PPO$_{62}$-*co*-*lin*PG$_1$-OH to -31 °C for the copolymer BnO-PPO$_{20}$-*co*-*lin*PG$_{30}$-OH after deprotection. We ascribe this to the additional interaction of the hydroxyl groups via hydrogen-bonding in the copolymers