Supplementary Material (ESI) for Soft Matter

Supporting Information to the Article

Smart Hydrogels Based on Double Responsive Triblock Terpolymers

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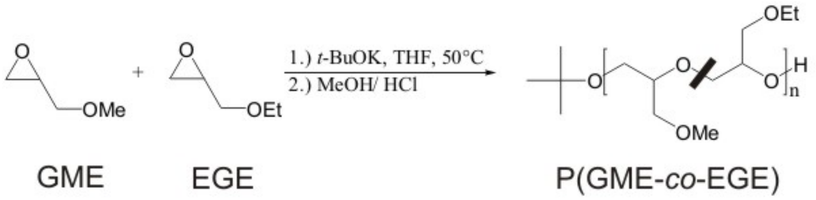
Determination of Reactivity Ratios for GME/EGE Copolymerization

The reaction scheme of the anionic ring-opening copolymerization of glycidyl methyl ether (GME) and ethyl glycidyl ether (EGE) is shown in Scheme S1. The molecular weights, polydispersity indices, and cloud points of all synthesized copolymers are summarized in Table S1. The commercially available lithium *tert*-butoxide initiator solution we used contains small amounts of the corresponding *tert*-butyl alcohol, as evidenced by gas chromatography. The alcohol can initiate the polymerization of epoxy monomers, too, since the proton exchange reaction between the alcohol and the alkoxide is much faster with respect to the propagation reaction. As a result, a lower molecular weight than theoretically expected is obtained. This has been observed in ethylene oxide polymerization, too, i.e. in this case no transfer reactions to the monomer occur, which might alternatively result in lower molecular weights.[1]



Scheme S1. Anionic ring-opening copolymerization of GME and EGE in THF using *t*-BuOK as initiator.

Table S1. Molecular characteristics and cloud points of GME/EGE copolymers.

Initiator	$[I]_0$ [mol/L]	$X_{0,\,GME}$ [mol%][a]	M_n (calc.) [g/mol]	M_n (SEC)[b] [g/mol]	M_w/M_n[b]	T_{cp}[c] [°C]
t-BuOK	$1.67 \cdot 10^{-2}$	0.15	4 900	5 200	1.07	19.1
t-BuOK	$1.70 \cdot 10^{-2}$	0.30	5 000	4 900	1.07	24.9
t-BuOK	$1.70 \cdot 10^{-2}$	0.50	5 000	5 400	1.06	32.1
t-BuOK	$1.77 \cdot 10^{-2}$	0.70	4 700	4 700	1.05	44.8
t-BuOK	$1.73 \cdot 10^{-2}$	0.85	4 900	4 500	1.09	57.1
t-BuOLi / *t*-BuP$_4$	$1.70 \cdot 10^{-2}$	0.50	5 000	3 300	1.09	32.9

a) molar fraction of GME in the initial monomer mixture
b) determined by THF-SEC using PS-calibration
c) the cloud point T_{cp} is defined as the intercept of the tangents at the onset of turbidity (2.5 g/L, 1 K/min)

The copolymerization was followed by gas chromatography (GC) of samples taken during the course of reaction. The area of each monomer peak divided by the area of the decane peak (internal standard) is proportional to the corresponding monomer concentration:

$$\frac{A(Monomer)}{A(Decan)} = A_{norm.}(Monomer) \;\Rightarrow\; \sim[Monomer].$$

For the FINEMAN-ROSS[2] approach samples were taken after approximately 10 % conversion ($[M] \approx [M]_0$) for each copolymerization and the molar fraction of GME (x_{GME}) in the copolymer was calculated using the equation:

$$x_{gme} = \frac{(1-R(GME)) \cdot X_{0,GME}}{(1-R(GME)) \cdot X_{0,GME} + (1-R(EGE)) \cdot X_{0,EGE}}$$

with $$R(GME) = \frac{A_{norm.}(GME)}{A_{0,norm.}(GME)} \qquad R(EGE) = \frac{A_{norm.}(EGE)}{A_{0,norm.}(EGE)}.$$

$X_{0,GME}$ and $X_{0,EGE}$ denote the molar fractions of GME and EGE in the initial monomer mixture, respectively.

According to the Fineman-Ross equation:

$$\frac{(f-1)F}{f} = r_1 \frac{F^2}{f} - r_2,$$

with F = $\frac{X_{0,GME}}{X_{0,EGE}}$, and f = $\frac{x_{GME}}{x_{EGE}}$, the reactivity rations $r_1 = r_{GME}$ and $r_2 = r_{EGE}$ were determined from the slope and the y-axis intercept, respectively, of the corresponding linear fit (Figure S1, Table S2). The quality factor of the linear fit is 0.997.

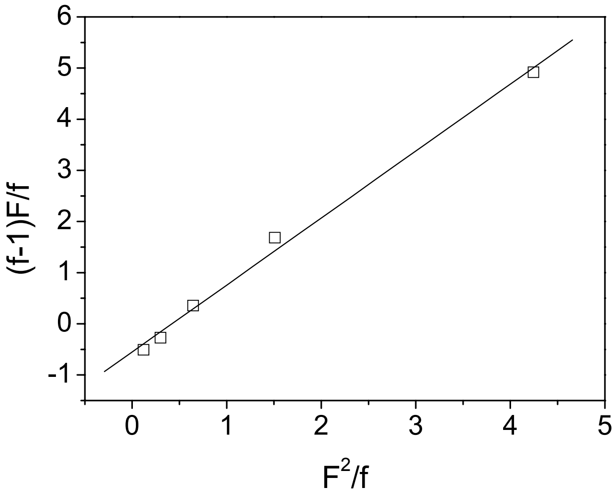


Figure S1. Fineman-Ross plot for GME/EGE copolymerization in THF with *t*-BuOK as initiator (50 °C).

The reactivity ratios were also calculated using the Skeist approach.[3] The advantage of this procedure is that it considers the change in the comonomer ratio when the reaction proceeds, making it possible to determine the reactivity ratios also from higher conversions in contrast to the Fineman-Ross method. Consequently, only one copolymerization experiment is necessary to calculate r_{GME} and r_{EGE}. For calculating the reactivity ratios following the Skeist approach one needs also the fraction of each monomer in the monomer mixture X_{GME} and X_{EGE} after different reaction times and the corresponding overall monomer conversion $x_p = 1-[M]/[M]_0$. These values were calculated using the following relations:

$$X_{GME}=\frac{R(GME)\cdot X_{0,GME}}{R(GME)\cdot X_{0,GME}+R(EGE)\cdot X_{0,EGE}}$$

$$1-\frac{M}{M_0}=1-\left(R(GME)\cdot X_{0,GME}+R(EGE)\cdot X_{0,EGE}\right)$$

From the solution of the integrated copolymerization equation, derived by Meyer et al.,[4, 5] the reactivity ratios were calculated numerically using the software MathCad 5.0:

$$1-\frac{M}{M_0}=1-\left[\frac{X_{GME}}{X_{0,GME}}\right]^{\frac{r_2}{1-r_1}}\left[\frac{X_{EGE}}{X_{0,EGE}}\right]^{\frac{r_1}{1-r_1}}\left[\frac{X_{0,GME}-\dfrac{1-r_2}{2-r_1-r_2}}{X_{GME}-\dfrac{1-r_2}{2-r_1-r_2}}\right]^{\frac{1-r_1r_2}{(1-r_1)(1-r_2)}}$$

The reactivity ratios calculated via the Fineman-Ross- and Skeist-approach for both initiating systems, *t*-BuOK and *t*-BuOLi/*t*-BuP$_4$, are summarized in Table S2.

Table S2. Reactivity ratios for GME/EGE copolymerization with two different initiating systems.

Initiator	r_{GME} / r_{EGE} (Fineman-Ross)	r_{GME}/ r_{EGE} (Skeist)
t-BuOK	1.31 / 0.55	1.42 / 0.53
t-BuOLi/*t*-BuP$_4$	-	1.33 / 0.72

Thermoresponsiveness of P(GME-*co*-EGE) Copolymers

Figure S2 shows the temperature dependent transmittance for aqueous solutions of P(GME-*co*-EGE) copolymers with varying composition.

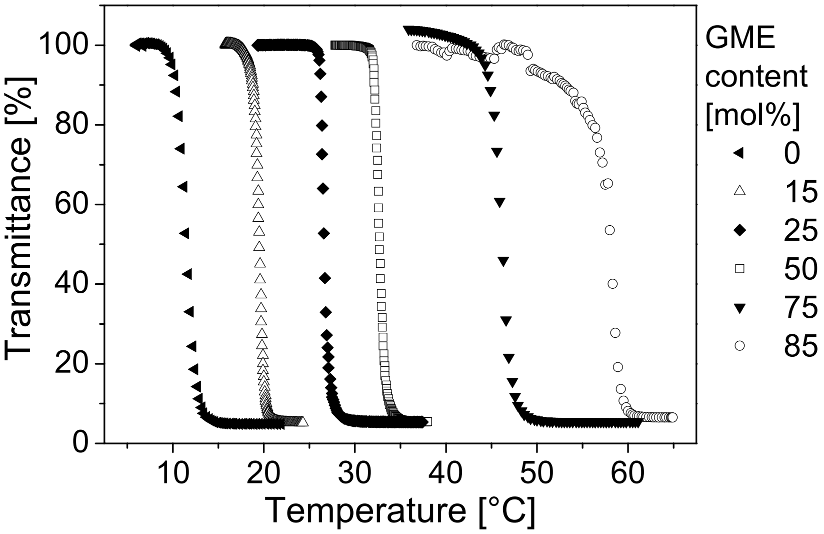


Figure S2. Transmittance vs. temperature for aqueous solutions of P(GME-*co*-EGE) in dependence of the GME content (2.5 g/L, 1 K/min).

REFERENCES:

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