

Supporting Information belonging to

Autonomous Flow Control by a Responsive Poly(2-hydroxyethyl acrylate) Organogel-Valve during the Aerobic Oxidation of Benzyl Alcohol

Jonah Hasse^a, Johannes Gmeiner^a, Gerrit A. Luinstra^{a} and Andreas Liese^b*

^aInstitute of Technical and Macromolecular Chemistry, University of Hamburg,

Bundesstraße 45, 20146 Hamburg, Germany

^bInstitute of Technical Biocatalysis, Hamburg University of Technology, Denickestr. 15, 21073

Hamburg, Germany

E-Mail: luinstra@chemie.uni-hamburg.de (G.A.L.)

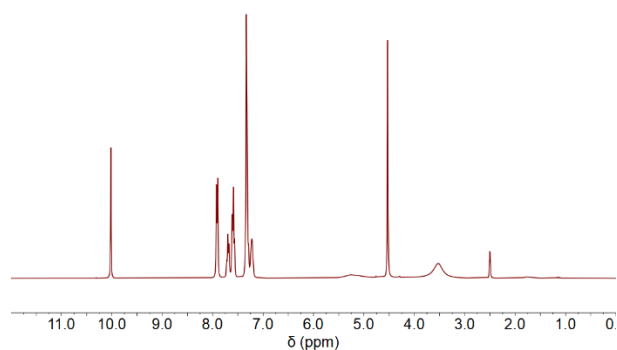


Figure S1. Representative ¹H-NMR-spectra of the reaction mixture for the aerobic oxidation of benzyl alcohol to benzaldehyde in DMSO-d₆. The molar conversion was quantified by integrating the benzylic methylene protons of benzyl alcohol ($\delta = 4.5$) and calculating the ratio relative to the

aldehyde proton of benzaldehyde ($\delta = 10.0$). $\delta = 10.0$ (s, 1H, -CHO, benzaldehyde), 7.9 (d, $J = 7.2$ Hz, 2H, Ar-H, benzaldehyde), 7.7 (t, $J = 7.2$ Hz, 1H, Ar-H, benzaldehyde), 7.6 (t, $J = 7.3$ Hz, 2H, Ar-H, benzaldehyde), 7.3 (d, $J = 4.4$ Hz, 4H, Ar-H, benzyl alcohol), 7.3 – 7.2 (m, 1H, Ar-H, benzyl alcohol), 4.5 (s, 2H, -CH₂-, benzyl alcohol).

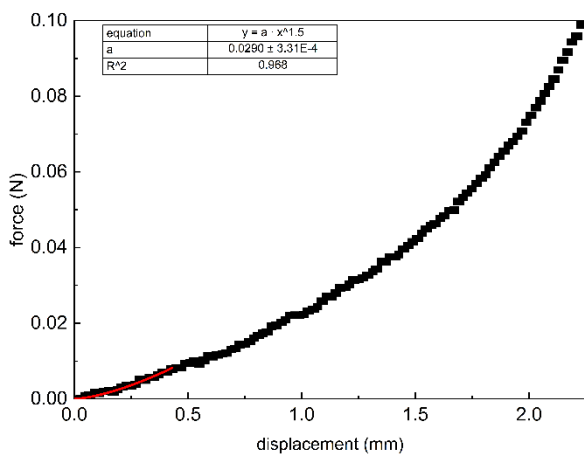


Figure S2. Force-displacement curve obtained from unconfined compression testing of HEA-20.

The Hansen Solubility Parameters (δ_d for dispersion, δ_p for polar, and δ_h for hydrogen bonding forces) of the PHEA network were estimated using the Hoftyzer Van Krevelen group contribution method. The calculation is based on the following equations:

$$\delta_d = \frac{\sum F_{di}}{V} \quad \delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad \delta_h = \frac{\sqrt{\sum E_{hi}}}{V}$$

where F_{di} is the dispersion component, F_{pi} is the polar component, E_{hi} is the hydrogen bonding energy per structural group, and V is the molar volume. The structural groups of the HEA repeating unit and their respective contributions are summarized in Table S1.

Table S1. Group contributions for the calculation of the HSP of PHEA according to Hoftyzer and Van Krevelen.

Structural Group	Count	F_{di} ((J/cm ³) ^{0.5} ·mol ⁻¹)	F_{pi} ((J/cm ³) ^{0.5} ·mol ⁻¹)	E_{hi} (J·mol ⁻¹)	V (cm ³ ·mol ⁻¹)
-CH ₂ -	3	270	0	0	16.1
-CH-	1	80	0	0	-1.0
-COO-	1	390	490	7000	18.0
-OH	1	210	500	20000	10.0
Sum		1490	990	27000	75.3

Based on these group contributions, the Hansen Solubility Parameters for PHEA were calculated. The thermodynamic interaction distance R_a between the PHEA network and the respective solvents was calculated using the classic Hansen equation.

$$R_a = \sqrt{4(\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2}$$

The calculated HSP for PHEA and the literature values for the utilized solvents, alongside the resulting interaction distances R_a , are summarized in Table S2.

Table S2. Hansen Solubility Parameters for PHEA and the solvents, and the calculated interaction distances R_a . (The literature values for the solvents were taken from the Hansen Solubility Parameters Handbook).

Material / Solvent	δ_d (MPa ^{0.5})	δ_p (MPa ^{0.5})	δ_h (MPa ^{0.5})	R_a to PHEA (MPa ^{0.5})
PHEA (19.8	9.3	18.9	-
Benzyl alcohol	18.4	6.3	13.7	6.6
Benzaldehyde	19.4	7.4	5.3	13.8

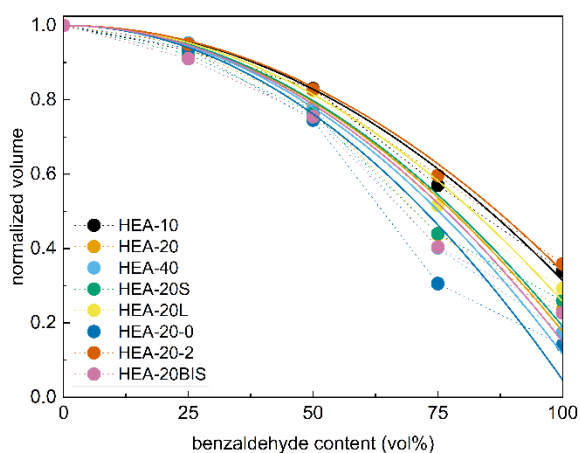


Figure S3. Relative bead volume as a function of the solvent composition. The experimental data are fitted to a quadratic model $y = 1 - C \cdot x^2$, with x as the fraction of benzaldehyde

Table S3. Fit parameters C and coefficients of determination R^2 for the solvent-dependent relative degree of swelling.

organogel	fit parameter C (10^{-5})	R^2
HEA-10	6.86	0.990
HEA-20-0	9.53	0.942
HEA-20	8.23	0.969
HEA-40	8.84	0.973
HEA-20-2	6.61	0.995
HEA-20S	8.09	0.956
HEA-20L	7.43	0.984
HEA-20BIS	8.50	0.950

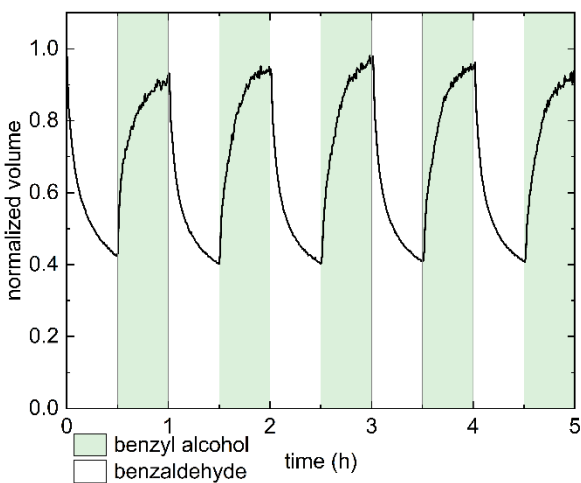


Figure S4. Cyclic exposure (30 min) of HEA-10 to benzyl alcohol (green underlay) and benzaldehyde.

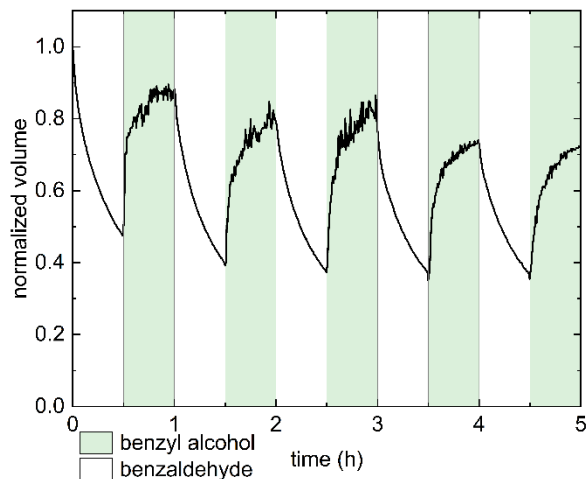


Figure S5. Cyclic exposure (30 min) of HEA-40 to benzyl alcohol (green underlay) and benzaldehyde.

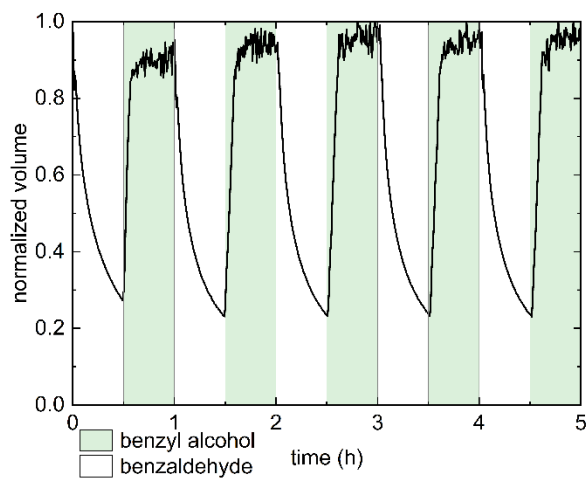


Figure S6. Cyclic exposure (30 min) of HEA-20-0 to benzyl alcohol (green underlay) and benzaldehyde.

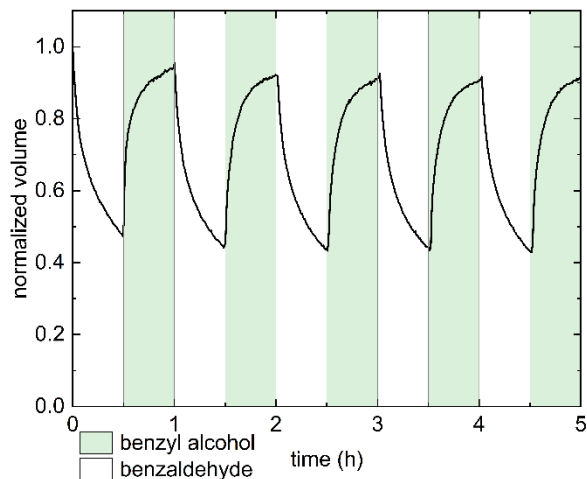


Figure S7. Cyclic exposure (30 min) of HEA-20-2 to benzyl alcohol (green underlay) and benzaldehyde.

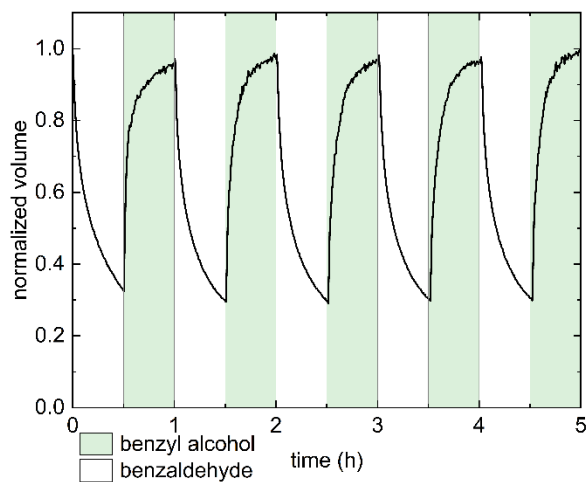


Figure S8. Cyclic exposure (30 min) of HEA-20BIS to benzyl alcohol (green underlay) and benzaldehyde.

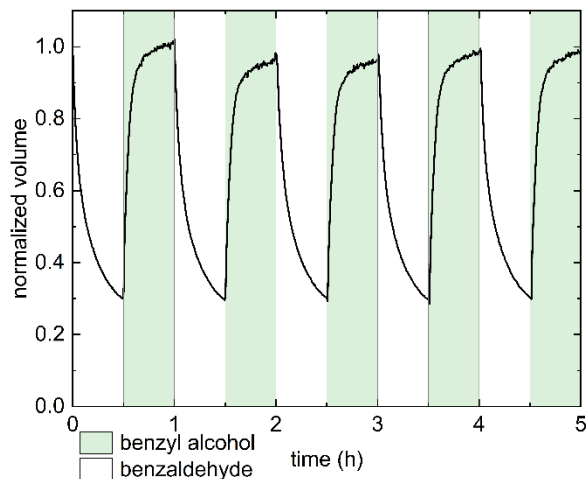


Figure S9. Cyclic exposure (30 min) of HEA-20S to benzyl alcohol (green underlay) and benzaldehyde.

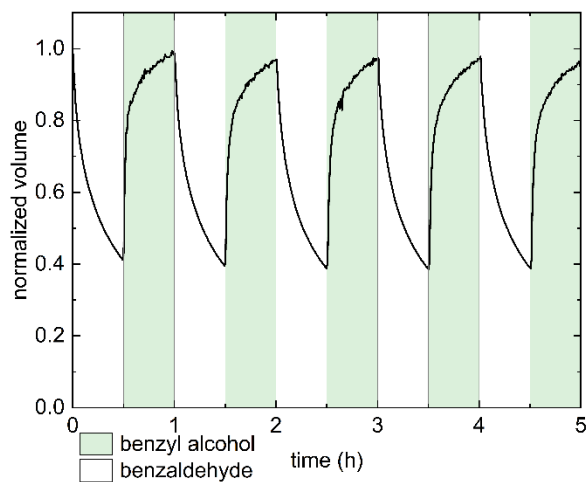


Figure S10. Cyclic exposure (30 min) of HEA-20L to benzyl alcohol (green underlay) and benzaldehyde.