

Electronic Supplemental Information for

Double-Crosslinked Supramolecular Grafted Hydrogels with Tunable Properties Based on Competition of Host-Guest Interactions

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Materials

Propargyl *p*-toluenesulfonate (*p*-OTs, Sigma-Aldrich, 95%) and methyl trifluoromethanesulfonate (MeOTf, Sigma-Aldrich, 98%) were purified by distillation and stored under an argon atmosphere prior to use. 2-methyl-2-oxazoline (MeOx, Sigma-Aldrich, 98%) was refluxed over CaH₂ and distilled under argon before use. 1-adamantanemethanol (Sigma-Aldrich, 99%), triethylamine (Sigma-Aldrich, ≥99%), 4-bromomethyl benzoyl bromide (Sigma-Aldrich, 96 %), piperazine (Sigma-Aldrich, 99%), 4-vinylbenzyl chloride (Sigma-Aldrich, 90 %), 2,6-di-*tert*-butyl-4-methylphenol (Sigma-Aldrich, ≥99%), sodium sulfate (Sigma-Aldrich, anhydrous, ≥99%), acetonitrile (Sigma-Aldrich, anhydrous, 99.8%), 2-methyl-2-oxazoline (Sigma-Aldrich, 98%), potassium carbonate (Sigma-Aldrich, anhydrous, ≥99%), propargyl *p*-toluenesulfonate (Sigma-Aldrich, ≥97 %), 6-monoazido-6-monodeoxy-β-cyclodextrin (Cyclodextrin-shop, ≥98%), sodium *L*-ascorbate (Sigma-Aldrich, ≥98%), copper(II) sulfate pentahydrate (Sigma-Aldrich, ≥98%), methyl trifluoromethanesulfonate (Sigma-Aldrich, ≥98%), acrylamide (Sigma-Aldrich, for northern and southern blotting, powder blend), *N,N,N',N'*-tetramethylethylenediamine (Sigma-Aldrich, 99%), *N,N'*-methylenebisacrylamide (Sigma-Aldrich, 99%), sodium peroxodisulfate (Sigma-Aldrich, ≥99%), *N,N*-dimethylformamide (Sigma-Aldrich, anhydrous, 99.8%), ethyl acetate (Acros, 99.5%), dichloromethane (Acros, ≥99 %), n-hexane (VWR Chemicals, ≥99%), chloroform (Acros, ≥99 %), methanol (VWR Chemicals, ≥99% and technical, ≥98.5%) and dichloromethane (VWR Chemicals, ≥99.5%) were used as received without further purifications.

SUPPORTING FIGURES

Table S1. Composition of monomers for the synthesis of poly(2-oxazoline) macromonomers (synthesis descriptions see experimental section)

Poly(2-methyl-2-oxazoline) macromonomers			
Ada-42	Initiator (1 eq.)	Monomer (40 eq.)	Vinylating agent
	I-1 0.1066 g, 0.29 mmol	MOXA 1 g, 11.75 mmol	V-1 0.29 g, 1.45 mmol
	Solvent	Reaction condition	
	ACN 3 mL	80 °C 8 h	

Alk-41	Initiator (1 eq.)	Monomer (40 eq.)	Vinylating agent
	propargyl <i>p</i> -toluenesulfonate 51 µL, 0.29 mmol	MOXA 1 g, 11.75 mmol	V-1 0.29 g, 1.45 mmol
	Solvent	Reaction condition	
CD-41	ACN 3 mL	70 °C 3.5 h	
	Alkynyl-macromonomer (1 eq.)	Azido- β -Cyclodextrin (1.2 eq)	Catalyst group
	Alk-41 250 mg, 0.069 mmol	95.91 mg, 0.083 mmol	sodium ascorbate 1.37 mg, 0.0069 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 1.72 mg, 0.0069 mmol
Me-19	Solvent	Reaction condition	
	DMF 2 mL	r.t. 72 h	
	Initiator (1 eq.)	Monomer (25 eq.)	Vinylating agent
Ada-27	methyl trifluoromethanesulfonate 32.13 µL, 0.47 mmol	MOXA 1 g, 11.75 mmol	V-1 0.29 g, 1.45 mmol
	Solvent	Reaction condition	
	ACN 3 mL	85 °C 1 h	
Alk-27	Initiator (1 eq.)	Monomer (25 eq.)	Vinylating agent
	I-1 0.1706 g, 0.47 mmol	MOXA 1 g, 11.75 mmol	V-1 0.29 g, 1.45 mmol
	Solvent	Reaction condition	
CD-26	ACN 3 mL	80 °C 6 h	
CD-26	Alkynyl-macromonomer (1 eq.)	Azido- β -Cyclodextrin (1.2 eq)	Catalyst group
	Alk-27 379 mg, 0.1445 mmol	183 mg, 0.1734 mmol	sodium ascorbate 3.81 mg, 0.0192 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 3.62 mg, 0.0145 mmol

	Solvent	Reaction condition		
	DMF 2 mL	r.t. 72 h		
Ada-61	Initiator (1 eq.)	Monomer (55 eq.)		Vinylating agent
	I-1 0.078 g, 0.21 mmol	MOXA 1 g, 11.75 mmol		V-1 0.29 g, 1.45 mmol
	Solvent	Reaction condition		
	ACN 3 mL	80 °C 4 h		
ALk-58	Initiator (1 eq.)	Monomer (55 eq.)		Vinylating agent
	propargyl <i>p</i> -toluenesulfonate 0.037 μL, 0.21 mmol	MOXA 1 g, 11.75 mmol		V-1 0.29 g, 1.45 mmol
	Solvent	Reaction condition		
	ACN 3 mL	70 °C 4.5 h		
CD-59	Alkynyl-macromonomer (1 eq.)	Azido-β-Cyclodextrin (1.2 eq)		Catalyst group
	Alk-58 369.2 mg, 0.075 mmol	101.7 mg, 0.09 mmol		sodium ascorbate 1.98 mg, 0.001 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 1.875 mg, 0.0075 mmol
	Solvent	Reaction condition		
	DMF 2 mL	r.t. 72 h		

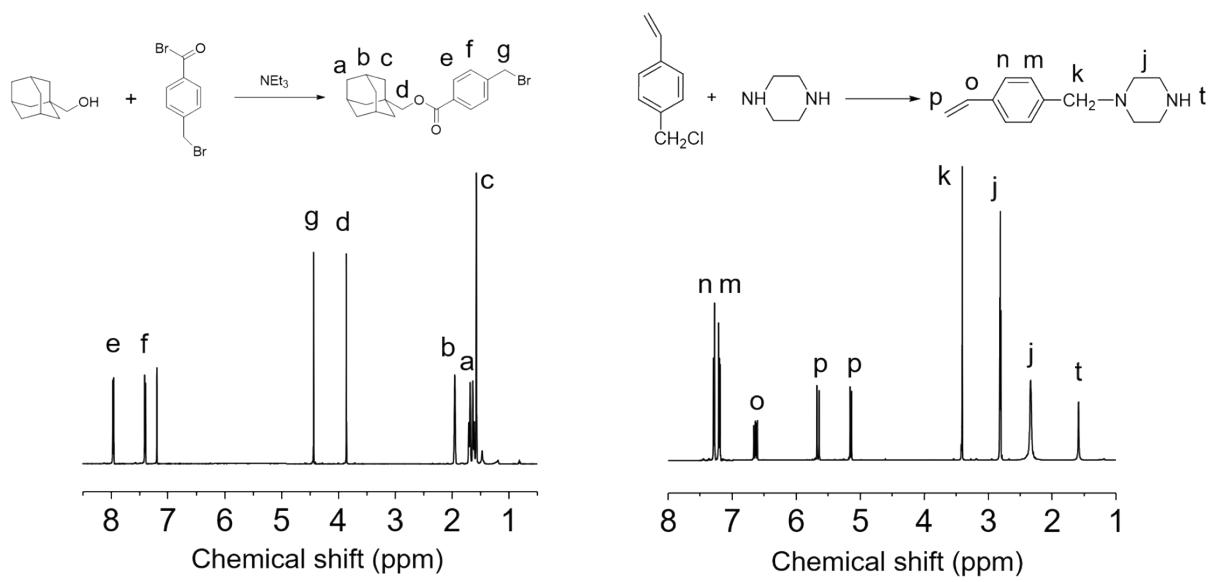


Figure S1. ^1H NMR spectra of adamantine-initiator (I-1, left) and vinylating agent 4-VBP (V-1, right) recorded in CDCl_3

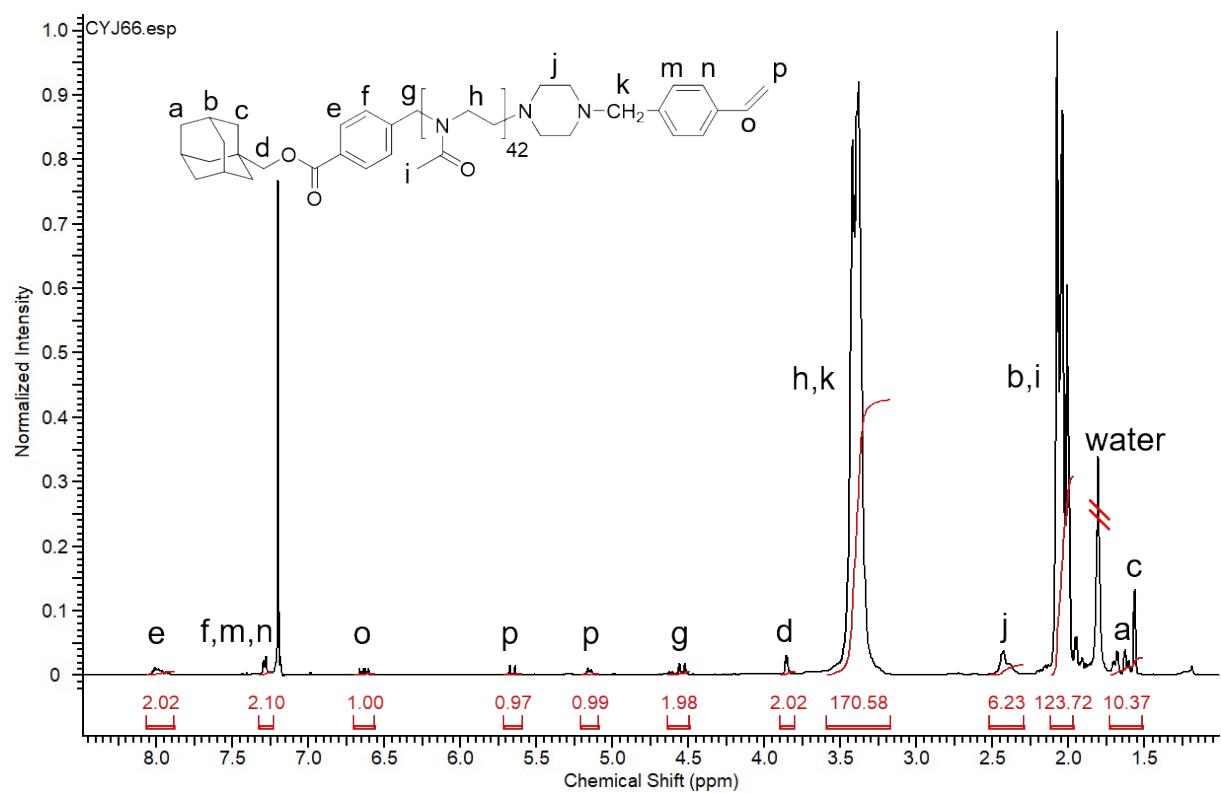


Figure S2. ^1H NMR spectra of polymer Ada-42 recorded in CDCl_3

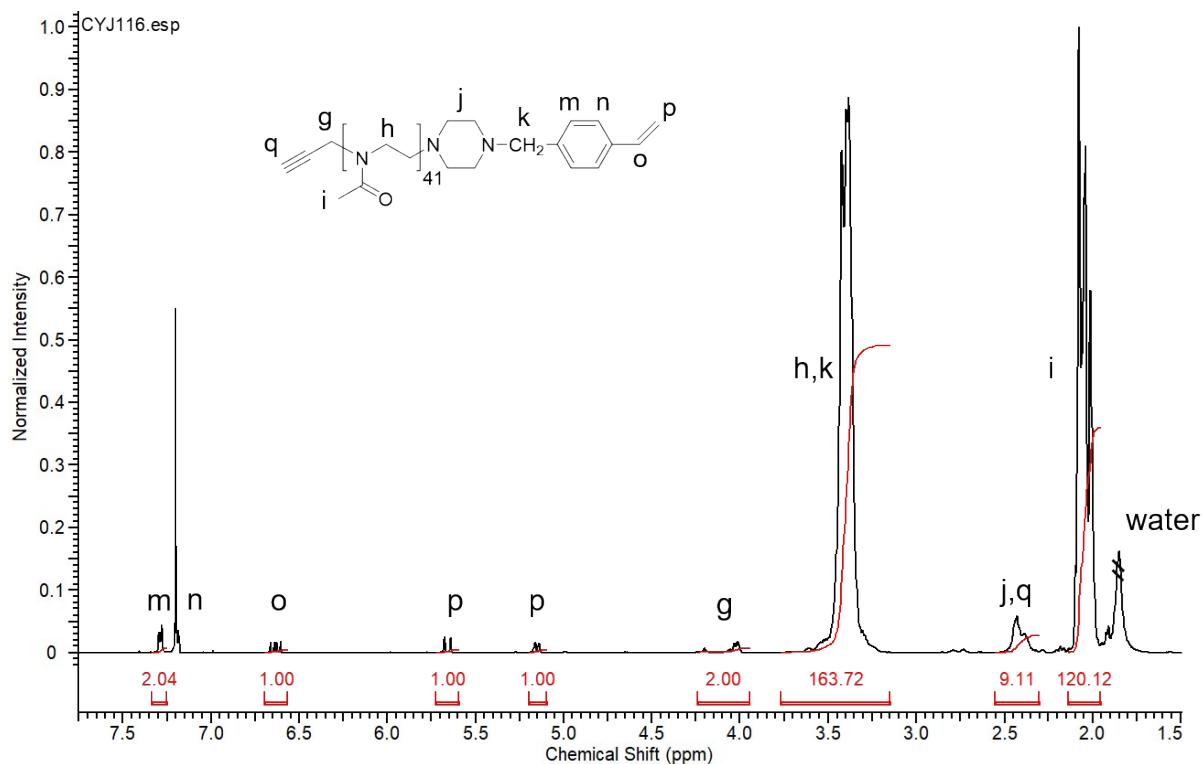


Figure S3. ^1H NMR spectra of polymer Alk-41 recorded in CDCl_3

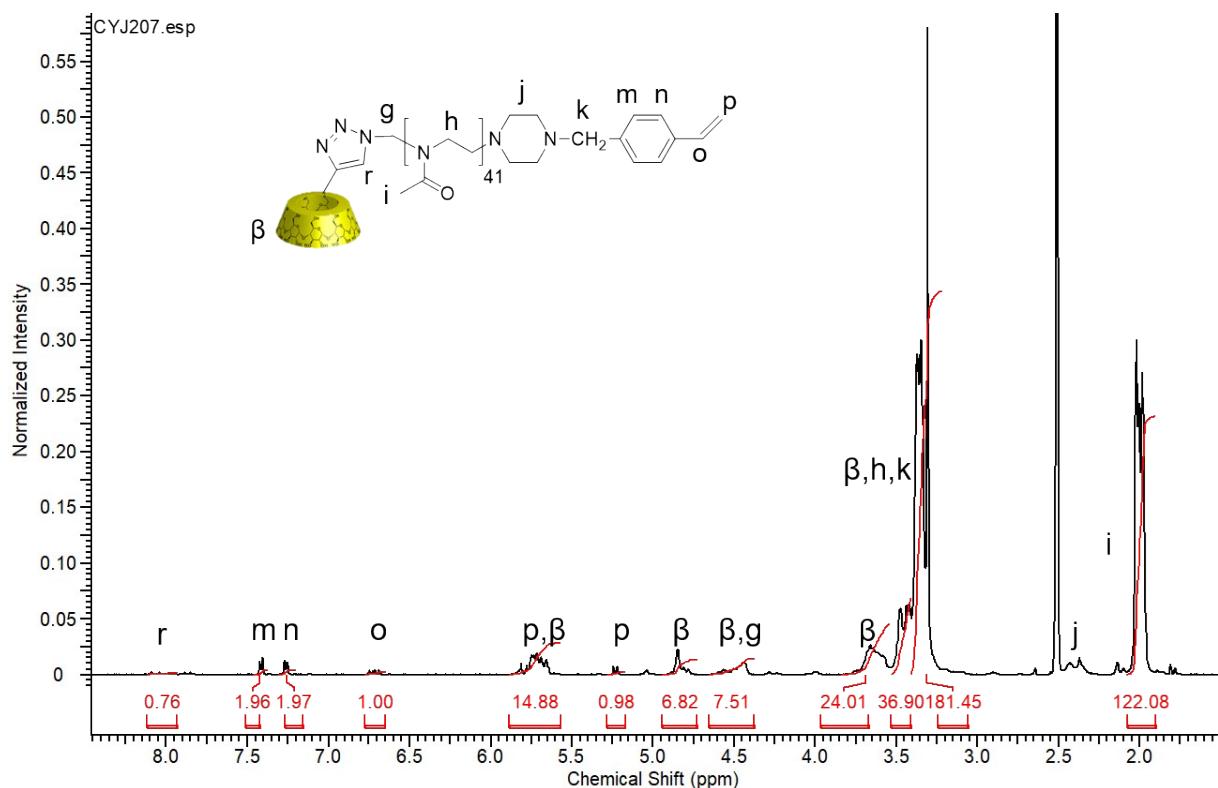


Figure S4. ^1H NMR spectra of polymer CD-41 recorded in DMSO-d_6 .

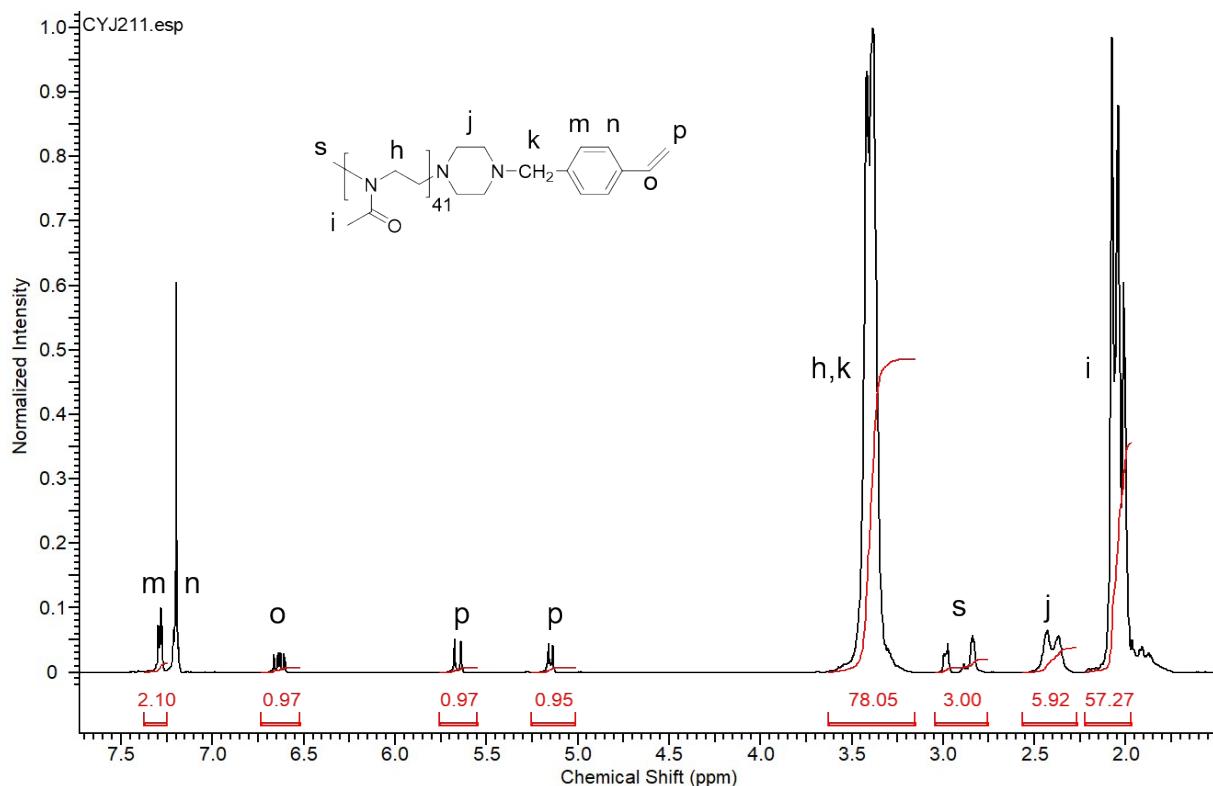


Figure S5. ^1H NMR spectra of polymer Me-19 recorded in CDCl_3

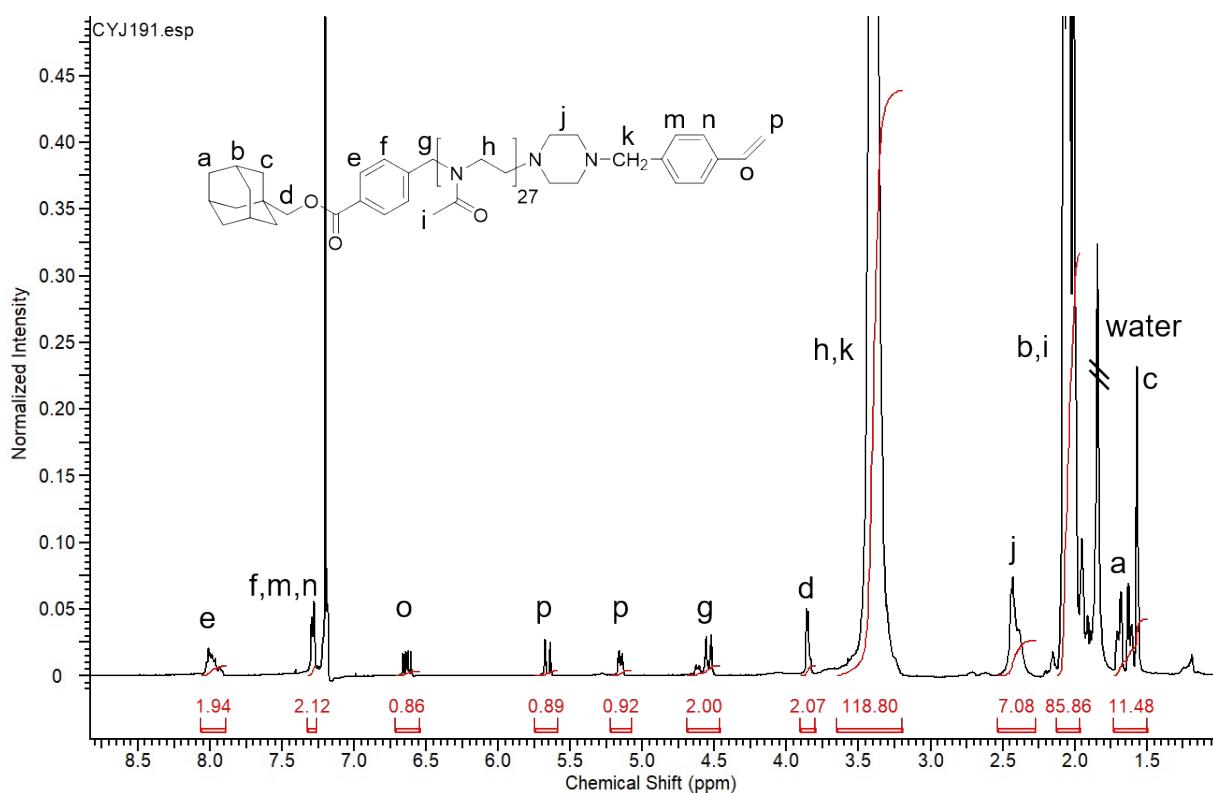


Figure S6. ^1H NMR spectra of polymer Ada-27 recorded in CDCl_3

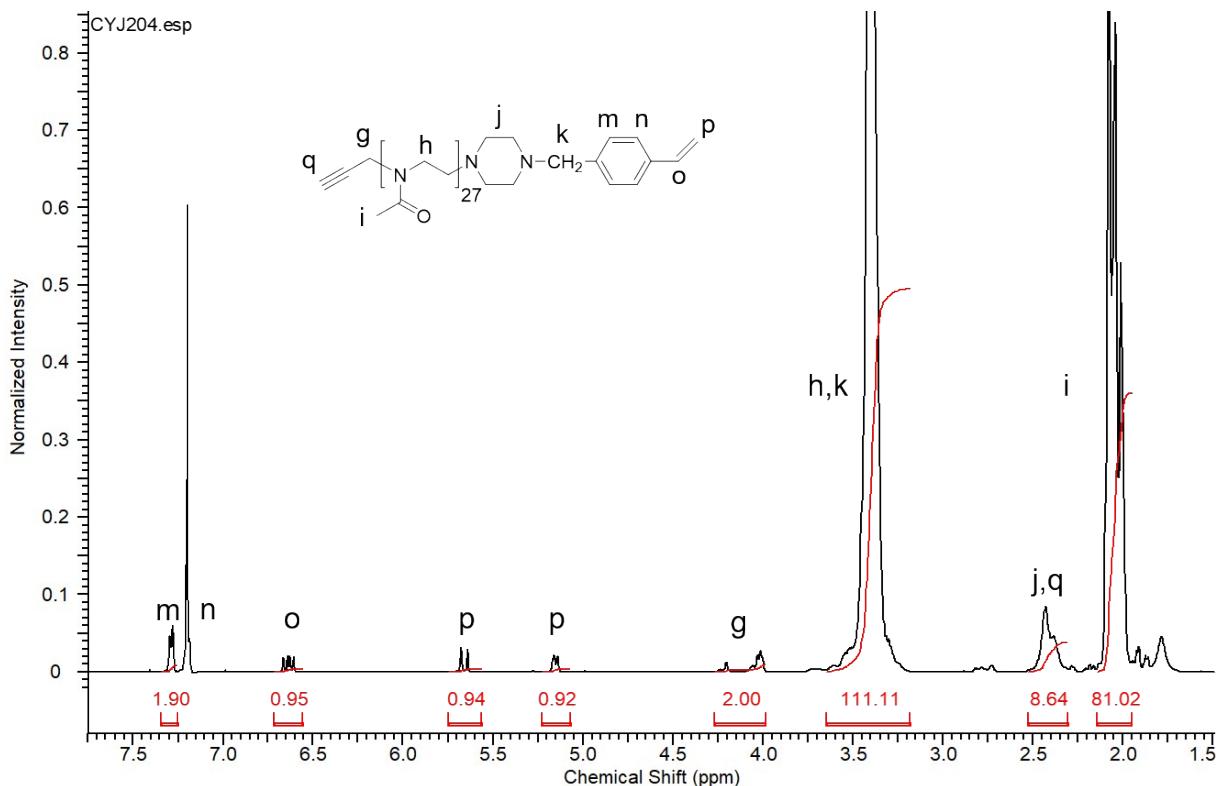


Figure S7. ^1H NMR spectra of polymer Alk-27 recorded in CDCl_3

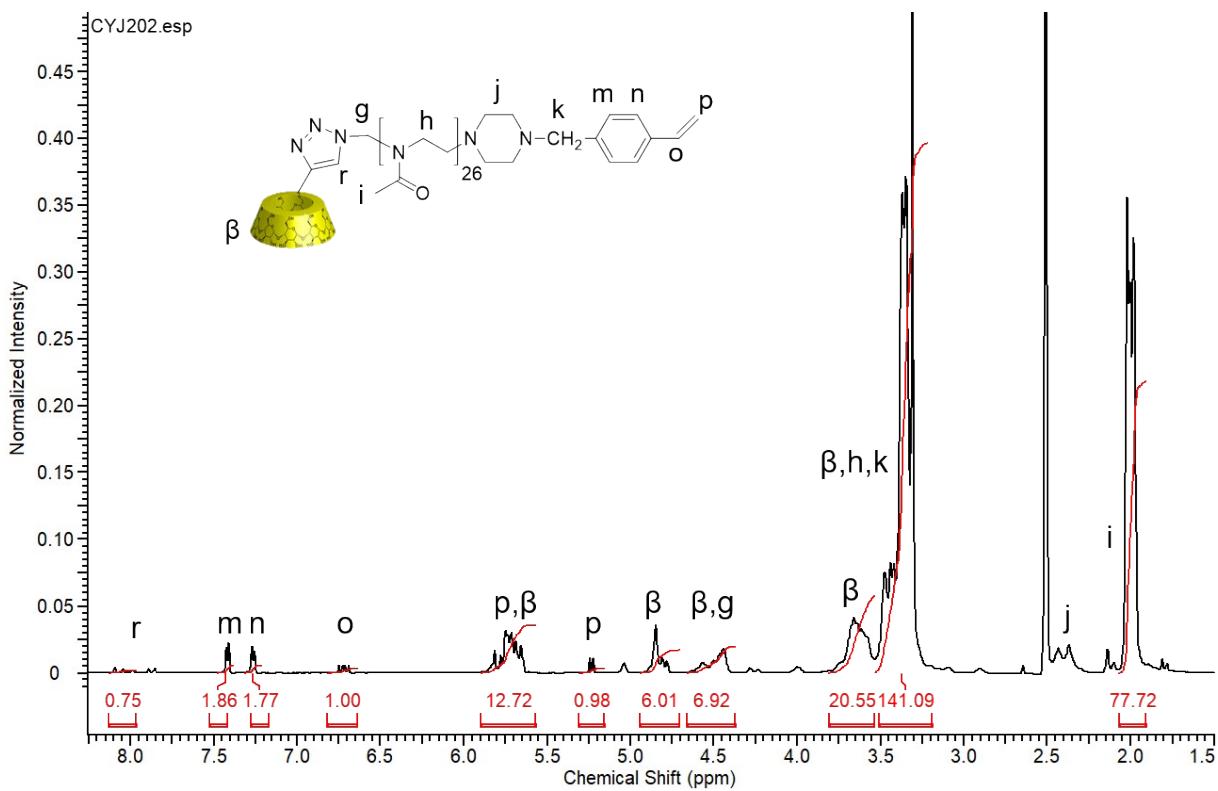


Figure S8. ^1H NMR spectra of polymer CD-26 recorded in DMSO-d_6 .

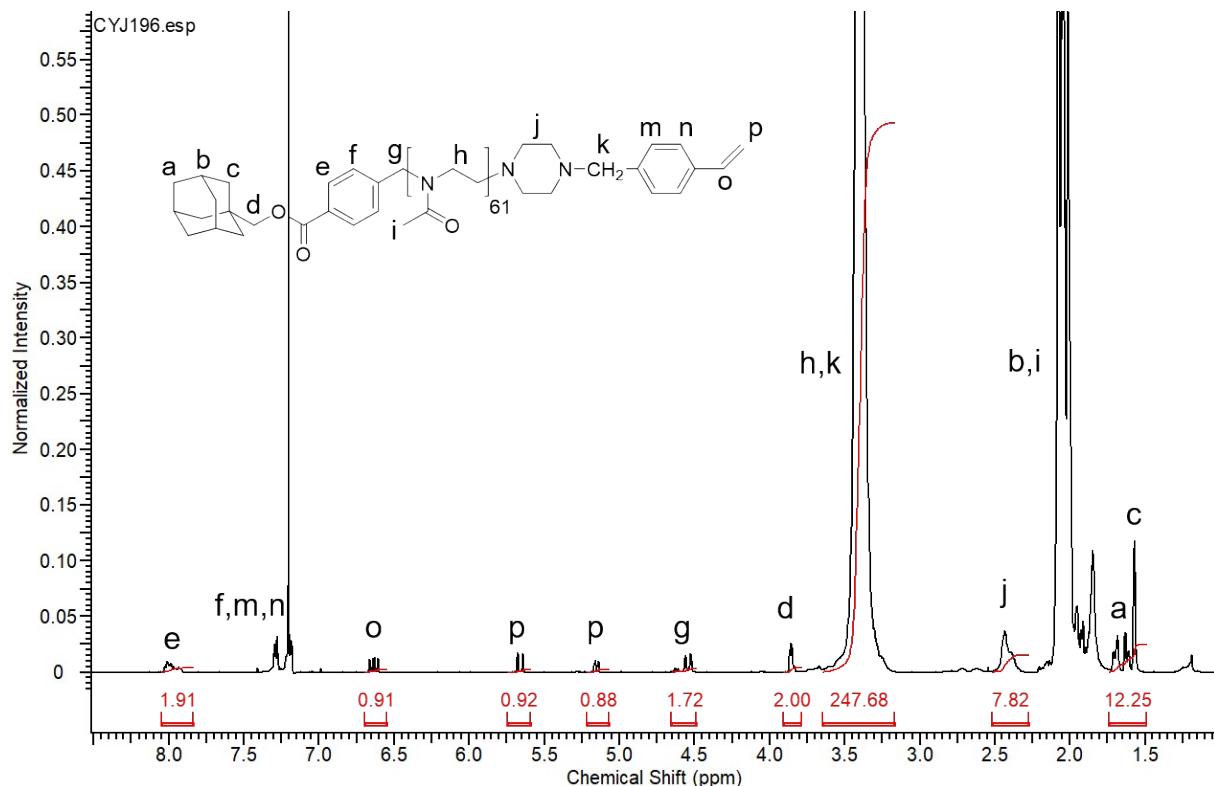


Figure S9. ^1H NMR spectra of polymer Ada-61 recorded in CDCl_3

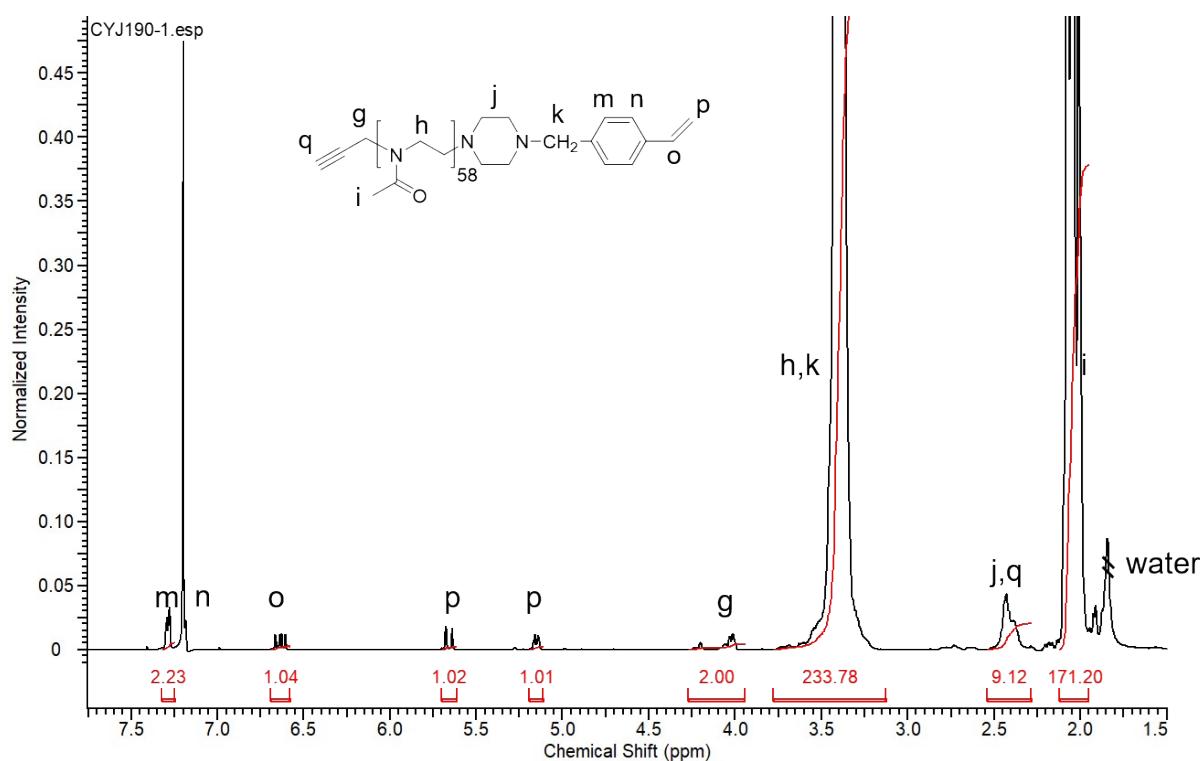


Figure S10. ^1H NMR spectra of polymer Alk-58 recorded in CDCl_3

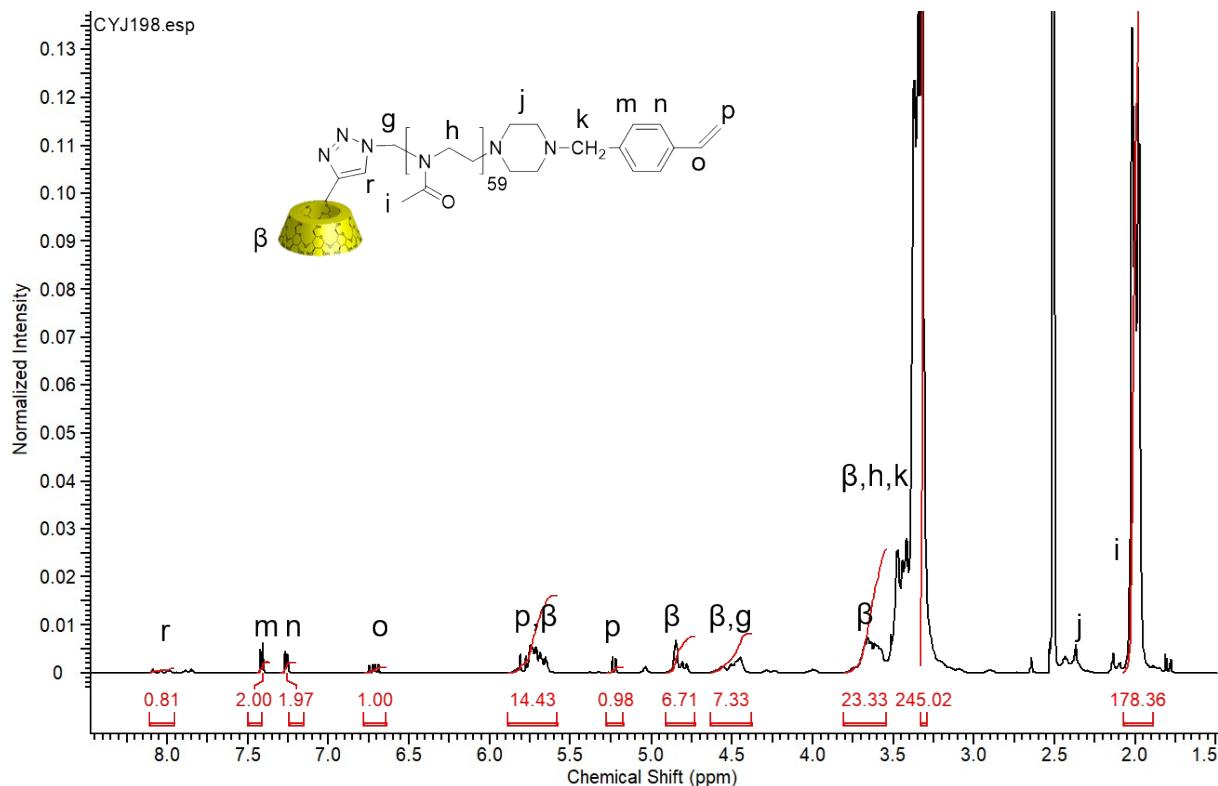
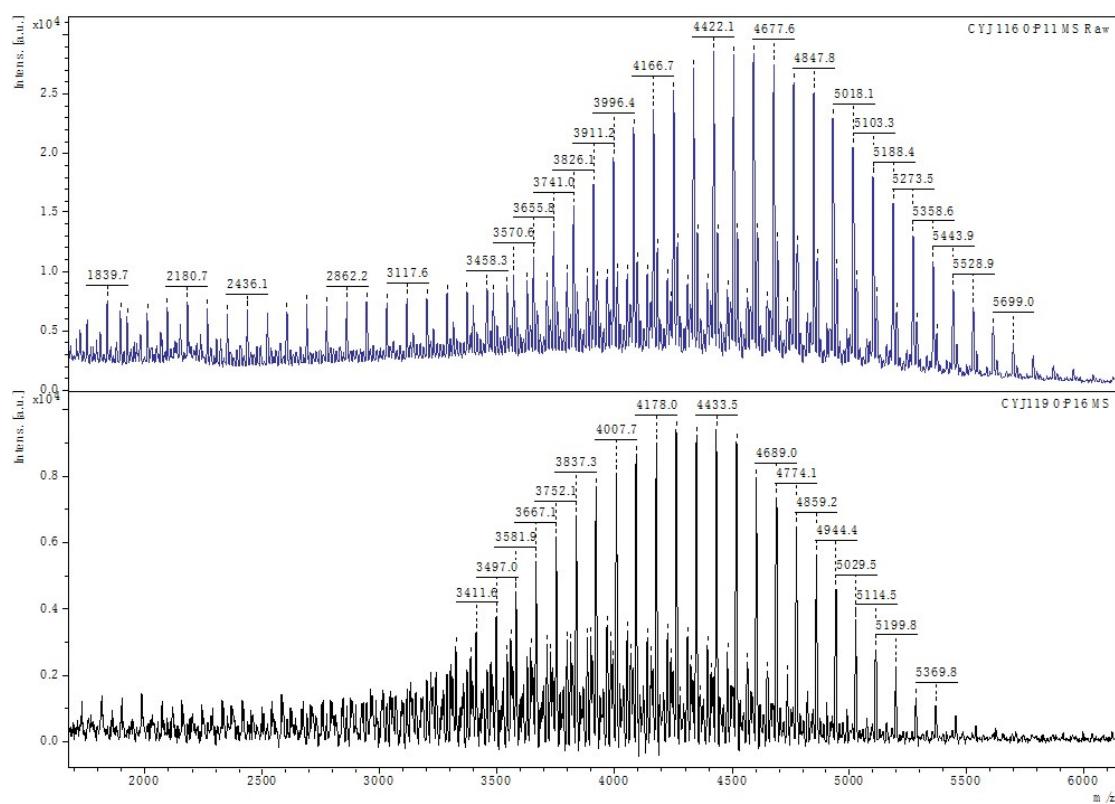


Figure S11. ^1H NMR spectra of polymer CD-59 recorded in DMSO-d_6 .



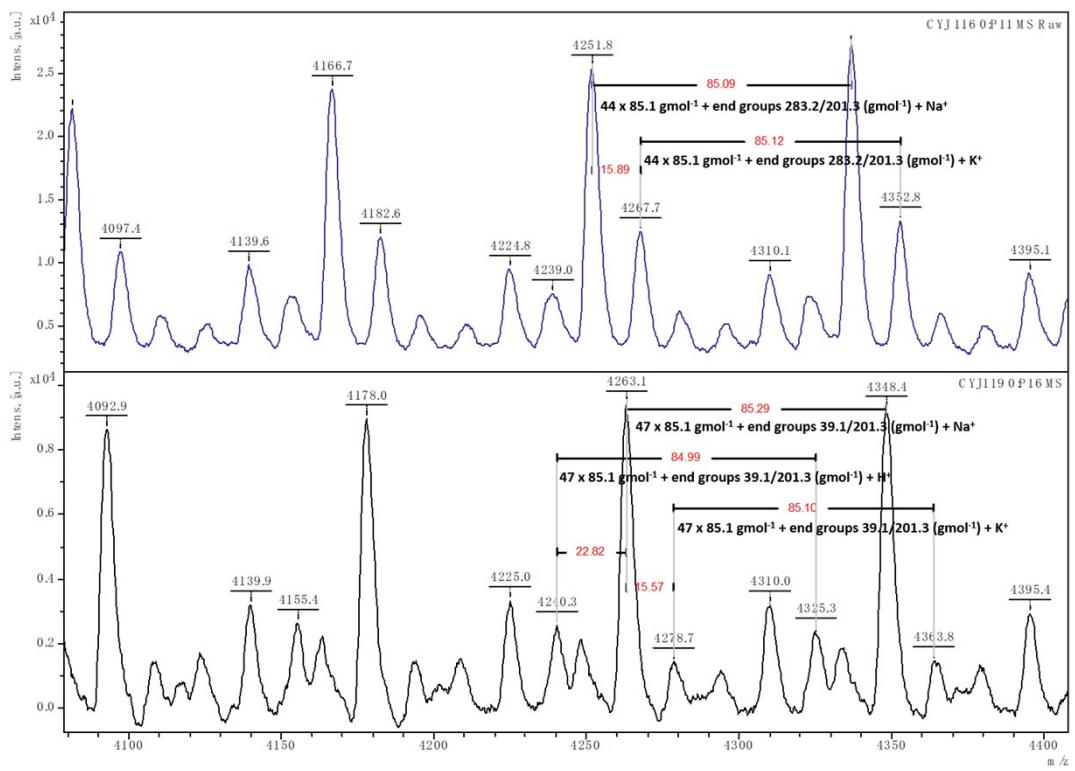


Figure S12. MALDI-TOF-MS spectra of Ada-42 (blue) and Alk-41 (black).

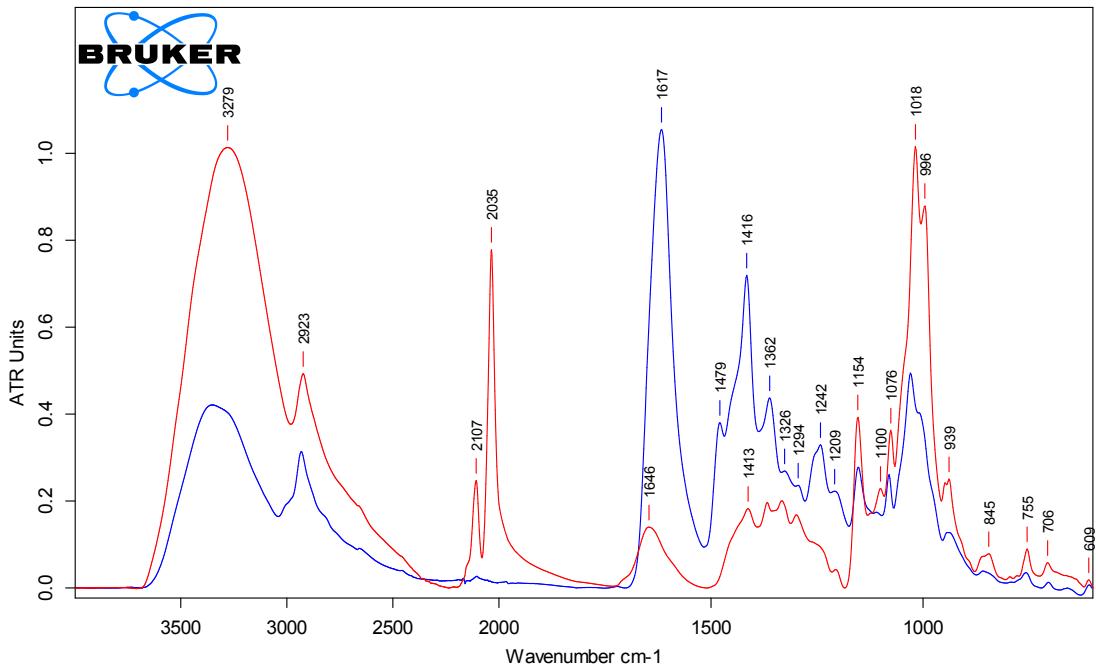


Figure S13. FT-IR spectra of CD-41 (blue line) compared with 6-monoazido-6-monodeoxy- β -cyclodextrin (red line).

Table S2. Composition of monomers for the synthesis of hydrogels (synthesis descriptions see experimental section)

Hydrogels			
H-AAm	Monomer	Cross-linker	Solvent
	Acrylamide 150 mg	BIS 1.626 mg	Water 1.282 mL
	Accelerator	Initiator	
	TMEDA 1.59 µL	NaPS 12.6 µL	
GH-19Me	Monomer	Cross-linker	Solvent
	Acrylamide 150 mg	BIS 1.626 mg	Water 1.282 mL
	Accelerator	Initiator	Macromonomer
	TMEDA 1.59 µL	NaPS 12.6 µL	Me-19: 40.09 mg
GH-25	Monomer	Cross-linker	Solvent
	Acrylamide 150 mg	BIS 1.626 mg	Water 1.282 mL
	Accelerator	Initiator	Macromonomer
	TMEDA 1.59 µL	NaPS 12.6 µL	Ada-27: 29.3 mg CD-26: 37.39 mg
GH-40	Monomer	Cross-linker	Solvent
	Acrylamide 150 mg	BIS 1.626 mg	Water 1.282 mL
	Accelerator	Initiator	Macromonomer
	TMEDA 1.59 µL	NaPS 12.6 µL	Ada-42: 40.97 mg CD-41: 50.86 mg
GH-60	Monomer	Cross-linker	Solvent
	Acrylamide 150 mg	BIS 1.626 mg	Water 1.282 mL
	Accelerator	Initiator	Macromonomer
	TMEDA 1.59 µL	NaPS 12.6 µL	Ada-61: 57.13 mg CD-59: 69.13 mg