Supporting Information for

From non-conventional ideas to multifunctional solvents inspired by green chemistry: A fancy or sustainabile macromolecular chemistry?

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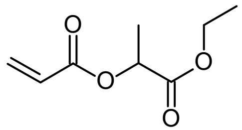
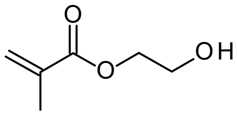
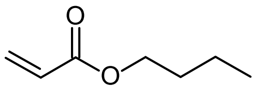
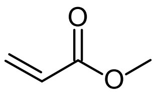
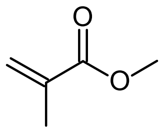
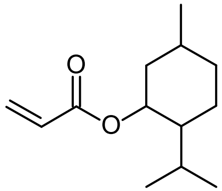
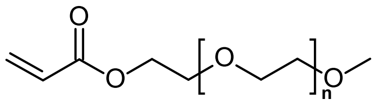
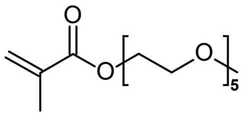
Table S1. Polymers synthesized in ethyl lactate as solvent

Monomer	Synthesis method	Reducing agent	Catalyst	Catalyst concentration [ppm]	Conv. [%]	$M_{n,theo}$ [g/mol]	$M_{n,app}$ [g/mol]	$Đ$	Ref
ELA 	SET-LPR [a, f, g)]	Cu^0 wire	-/Me_6TREN	n/a	86	14,730	16,500	1.18	1
					90	15,520	18,700	1.19	
					83	14,050	14,330	1.22	
					81	14,140	14,200	1.26	
HEMA 	LPR [b, d, g)]	-	AChI	10,000	59	12,000	11,000	1.16	2
*n*BA 	LPR [c, d, i)]	-	BChI	40,000	48	6,100	6,000	1.30	2
	SET-LPR [a, e, h)]	Cu^0 wire	-/Me_6TREN	n/a	80	6,800	6,800	1.20	3
					80	21,850	23,000	1.18	
MA 	ARGET ATRP [a, f, h)]	AsAc	$Cu^{II}Br_2$/ Me_6TREN	225	78.1	15,100	16,400	1.14	4
		AsAc-Na			77.1	15,000	16,000	1.14	
		$Na_2S_2O_4$			68.5	13,300	14,200	1.13	
		$NaHSO_3$			10.8	2,300	2,400	1.16	
		$Na_2S_2O_7$			16.6	3,400	3,500	1.15	
	SET-LPR [a, e, h)]	Cu^0 wire	-/Me_6TREN	n/a	88	5,000	4,800	1.29	3
					90	43,000	43,000	1.17	

MMA 	LPR [b, d, g)]	-	BChI	10,000	99	21,000	14,000	1.23	2
MnA 	SET-LPR [a, e, h)]	Cu^0 wire	-/Me_6TREN	n/a	83	8,890	7,980	1.42	5
OEOMEA 	SET-LPR [a, e, h)]	Cu^0 wire	-/Me_6TREN	n/a	88	18,300	18,300	1.29	3
PEGMA 	LPR [b, d, g)]	-	AChI	10,000	89	31,000	15,000	1.19	2

[a)]T = 25-30°C [b)]T = 50-60°C [c)]T = 100°C [d)] chain extension reaction [e)] methyl 2-bromopropionate (MBP) as initiator [f)] ethyl α-bromoisobutyrate (EBiB) as initiator [g)] t = 1-4 h [h)] t = 5-8 h [i)] t = 48 h

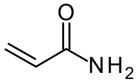
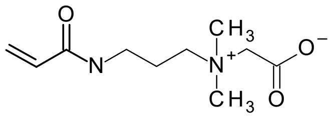
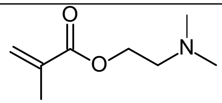
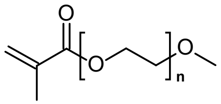
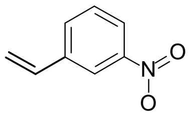
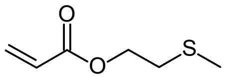
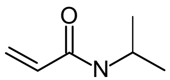
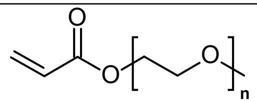
Table S2. Summary of polymerizations conducted in alcoholic beverages as solvents

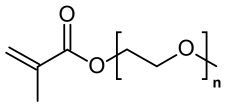
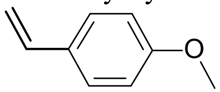
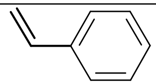
Method	Type	Solvent	Alc. [%]	Reducing agent	Monomer	Catalyst	Catalyst concentration [ppm]	$M_{n,th}$ [g/mol]	$M_{n,app}$ [g/mol]	Đ	Ref.
ARGET [a, d, g]	Beer	Lemon beer 0%	0	AsAc, citric acid	DMAEMA	$Cu^{II}Br_2$/TPMA	100	29,600	35,600	1.49	6
		Lemon beer 3.5%	3.5					29,800	40,100	1.64	
photoATRP [a. d. g]	Spirit	Rectified spirit 95%	95	lightwave 460 nm	DMAEMA	$Cu^{II}Br_2$/TPMA	300	84,500	75,000	1.14	7
	Vodka	Bison Grass Vodka	37.5					127,800	98,800	1.17	
		Wódka Parkowa	38					130,000	101,000	1.18	
		Żołądkowa de Luxe	40					119,800	84,000	1.17	
RAFT [b. e. i]	Alcopop	Smirnoff Ice	5	[l]	HEA	[l]	[l]	296,000 [k]	34,000	<1.1	8
	Baesk	Nepson's Maloert	35					212,000 [k]	22,000	<1.1	
	Beer	Lager - Miller High Life Light	4.6					299,000 [k]	30,000	<1.1	
		Stout - Guinness Draught	4.3					296,000 [k]	29,000	1.1	
		Ale - Shinner Birthday Beer 108	5					280,000 [k]	34,000	1.2	
	Bourbon	Rowan's Creek	40					259,000 [k]	26,000	<1.1	
	Brandy	Maxime Trijol Cognac Special						243,000 [k]	22,000	<1.1	
	Cider	Angry Orchard	5					302,000 [k]	32,000	1.2	
	Gin	Death's Door Gin	47					274,000 [k]	34,000	<1.2	
	Hot Toddy	Hot Toddy	20					280,000 [k]	24,000	<1.1	
	Raki	Efe	45					259,000 [k]	33,000	<1.1	
	Red wine	Black Box Cabernet Sauvignon	13.5					287,000 [k]	33,000	<1.1	
	Tequila	Espolón Tequila Blanco	40					280,000 [k]	27,000	<1.1	
	Vodka	ZYR Vodka						296,000 [k]	33,000	<1.1	
	Whiskey	House of Stuart						274,000 [k]	23,000	<1.1	
		James Irish Whisky						280,000 [k]	29,000	<1.1	
SARA ATRP. ARGET ATRP [b. d]	Red wine	Merlot	15	AsAc, thiosulphtes	nBA [j]	$Cu^{II}Br_2$/TPMA	300	10,700	17,700	1.16	9
					nBMA [h]			7,300	8,200	1.3	
					tBA [j]			9,700	8,300	1.31	

SET-LRP [c. f. g)]	Beer	Alpha Beer	5	Cu^0	NIPAM	Cu^IBr/ Me_6TREN	20000	2,400 [k)]	3,200	1.06	10
		Brains Rev. James	4.5					2,500 [k)]	3,200	1.1	
		Guinness	4.2					2,500 [k)]	3,600	1	
		Karhu	4.6					2,500 [k)]	3,600	1.07	
		Krombacher	4.7					1,800 [k)]	3,000	1.28	
		McEwan's Champion	7.3					2,500 [k)]	3,400	1.09	
		Singha	5					2,500 [k)]	3,300	1.12	
		Tsingtao	4.7					2,500 [k)]	3,500	1	
		Ale - Bank's Bitter	3.8					2,500 [k)]	3,900	1	
		Ale - Bank's Mild	3.5					2,500 [k)]	4,000	1	
		Ale - Leffe	6.6					2,300 [k)]	3,000	1.1	
	Brandy	Homemade Brandy	n.d.					2,400 [k)]	3,000	1.07	
		Kingston Black Apple Apperitif	18					2,200 [k)]	1,900	1	
		Napoleon Brandy Bordeaux 1973	40					2,100 [k)]	3,900	1.05	
		Tsipouro	40					2,400 [k)]	3,200	1.06	
	Cider	Burrow Hill Cider	6					1,700 [k)]	2,300	1	
	Liqueur	Morand Abricotine	43					2,400 [k)]	2,800	1.14	
		Primm's	25					2,500 [k)]	3,900	1	
		Verveine Verte	55					1,600 [k)]	1,600	1	
	Raki	Yeni	45					2,500 [k)]	5,000	1.06	
	Red wine	Chateau Laubes Bordeaux 2009	12.5					2,200 [k)]	2,600	1	
	Tequila	Jose Cuervo Gold Tequila	38					9,300 [k)]	9,900	1.08	11
	Vodka	Absolut Elyx Vodka	40					2,100 [k)]	3,000	1.08	10
		Imperial Vodka	37.5					2,500 [k)]	4,000	1.05	
		Ouzo	38					1,800 [k)]	3,800	1.07	
	Whiskey	A'Bunadh Single Malt	59					2,500 [k)]	2,800	1.08	

[a)] T = RT. [b)] T = 45-65°C. [c)] T = 0°C. [d)] ethyl a-bromoisobutyrate (EBIB) as initiator. [e)] 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (Va-044) as initiator. [f)] , 3-dihydroxypropyl 2-bromo-2-methylpropanoate as initiator. [g)] t = 0-1.5 h. [h)] t = 5 h. [i)] t = 12 h. [j)] t = 26-53 h. [k)] calculated basing on information provided in article. [l)] not applicable – other RAFT parameters: chain transfer agent (CTA) - 2-(propylthiocarbonothioylthio)-2-methylpropionoic acid (PPA) (10-30 mg ml^{-1} in 40% v/v aqueous ethanol). degassing system: GO_x (16 mg ml^{-1} in PBS). glucose (1 M in DI water)

Table S3. Summary of monomers polymerized using PBS in the role of solvent. T = 25 - 37°C

Monomer	Method	Reducing agent	Catalyst	Catalyst concentration [ppm]	$M_{n.th}$	$M_{n.app}$	Đ	Result	Ref.
 AM[e, m)]	photoCRP	lightwave 365 nm	$Cu^{II}Br_2$/ Me_6TREN	6	c)	c)	c)	Protein-polymer brushes hybrid	12
CBAA [e, h)] 	classic ATRP	b)	$Cu^{II}Br_2$/ $Me_4Cyclam$	3,955	b)	b)	b)	Antifouling polymer brushes	13
 DMAEMA [e, m)]	photoCRP	lightwave 365 nm	$Cu^{II}Br_2$/ Me_6TREN	6	c)	c)	c)	Protein-polymer brushes hybrid	13
 MeOEGMA [e,i)]	classic ATRP	b)	$Cu^{II}Br_2$/BPY	96,637	b)	b)	b)	Antifouling polymer brushes	13
 *m*-Nitro styrene [m)]	photoCRP	lightwave 365 nm	$Cu^{II}Br_2$/ Me_6TREN	750	c)	c)	c)	Protein-polymer brushes hybrid	12
MSEA [f)] 	eATRP [j)]	current	$Cu^{II}Br_2$/ Me_6TREN	5,000	6,800	8,000	1.34	DNA-polymer brushes hybrid	14
NIPAM 	ARGET ATRP [f, j)]	NaAsc	Hemozoin	c)	c)	47,000	3.8	Hemozoin detection	15
			Hemoglobin	c)	c)	c)	c)	Hemoglobin detection	16
	SET-LRP [a,g,k)]	Cu^0	Cu^IBr/ Me_6TREN	10,000	8,526 [d)]	9,600	1.29	Synthesis in close to biological conditions	11
					9,346 [d)]	9,700	1.21		
 OEOA [e, m)]	photoCRP	lightwave 365 nm	$Cu^{II}Br_2$/ Me_6TREN	6	c)	c)	c)	Protein-polymer brushes hybrid	12
OEOMA	AGET	AsAc	$Cu^{II}Br_2$/TPMA	4,405	77,000 [l)]	93,000	1.12	Protein-polymer brushes	17

	ATRP [e)]				75,000 [m)]	83,000	1.19	hybrid	
	classic ATRP [e)]	-	$Cu^{II}Cl_2$/BPY		36,000 [l)]	28,000	1.17		
					43,000 [m)]	50,000	1.26		
	*e*ATRP [f, n)]	current	$Cu^{II}Br_2$/TPMA	2,000	10,400	7,800	1.37	DNA-polymer brushes hybrids	14
					74,600	63,200	1.39		
				1,000	24,200	18,400	1.36		
				400	38,000	27,000	1.59		
p-Methoxy styrene [m)] 	photoCRP	lightwave 365 nm	$Cu^{II}Br_2$/ Me_6TREN	750	[c)]	[c)]	[c)]	Protein-polymer brushes hybrid	12
 Styrene [e,m)]	photoCRP	lightwave 365 nm	$Cu^{II}Br_2$/ Me_6TREN	6	[c)]	[c)]	[c)]	Protein-polymer brushes hybrid	12

[a)] T = 0°C, [b)] not applicable, [c)] not determined, [d)] calculated basing on information provided in article, [e)] t = 2-6 h, [f)] t $\leqslant$ 1 h, [g)] t = 24 h, [h)] chain extension reaction, [i)] ω-mercaptoundecyl bromoisobutyrate (MUBIB) as initiator, [j)] 2-hydroxyethyl 2-bromoisobutyrate (HEBIB) as initiator, [k)] 3-dihydroxypropyl 2-bromo-2-methylpropanoate as initiator, [l)] poly(ethylene oxide) (PEO) as initiator, [m)] modified bovine serum albumin (BSA) as initiator, [n)] poly(ethylene glycol) α-bromoisobutyrate (PEG2kiBBr) as initiator

Table S4. Linear block copolymers obtained in various solvents.

Method	Solvent	Number of blocks	Block copolymers	Ref
Organocatalysed LRP	Ethyl lactate (EL)	2	P(MMA-*b*-PEGMA), P(MMA-*b*-HEMA), P(PEGMA-*b*-MMA)	2
RAFT	2-Methyltetrahydrofuran (2-MeTHF)	2	P(PEGMA-*b*-LA_{25}) P(HEMA-*b*-LA_{25})	18
SARA ATRP	Cyclopentyl methyl ether (CPME)/DMSO = 70/30 (v/v)	3	P(MA-*b*-VC-*b*-MA)	19
	L-Menthol, Thymol	2	P(MA-*b*-HEA) P(MA-*b*-OEOA) P(DMAEMA-*b*-HEA) P(MA-*b*-HEA-*b*-BA)	20
SET-LRP	Blood (sheep) serum	2	P(NIPAM)-*b*-(DMAm)	21
	H_2O	3	P(NIPAM-*b*-HEA-*b*-$PEGA_{480}$)	**11**

Table S5. Cost of conventional and non-conventional solvents described in articles.

Solvent	**Price [$/L]**
Acetone	84
N,*N*-Dimethylformamide (DMF)	120
Tetrahydrofuran (THF)	155
Toluene	94
1,3-Dimethyl-2-imidazolidinone (DMI)	315
γ-Valerolactone	134
γ -Butyrolactone	132
γ-Caprolactone	1346
γ-Octanolactone	2933
Cyclopentyl methyl ether (CPME)	226
Ethyl lactate (EL)	102
Tetraethylene glycol dimethyl ether (TEGME)	156
2-Methyltetrahydrofuran (MeTHF)	260
Ultrapure water	601
Distilled water	12
Tap water (Poland)	0.0014
Seawater	9
Lemon extract (commercial)	74
Beer	1.3-7.5
Bourbon	64
Brandy	27-70
Cider	4-6.5
Gin	51
Liqueur	24-79
Raki	34
Rectified spirit	26

Red wine	8
Tequila	33
Vodka	18-49
Whisky	10-79
Lysogeny broth	80
Fetal bovine serum (pure) (FBS)	1530
Calf serum (pure) (CS)	151.6
Dulbecco's modified eagle's medium (DMEM)	56.4

Prices of chemical compounds were taken from Sigma Aldrich website, seawater from www.naturalseawatersupplier.co.uk, tap water estimated in https://www.waternewseurope.com/water-prices-compared-in-36-eu-cities/ for Poland and alcoholic beverages from https://www.wine-searcher.com.

REFERENCES

1. N. Bensabeh, A. Moreno, A. Roig, O. R. Monaghan, J. C. Ronda, V. Cádiz, M. Galià, S. M. Howdle, G. Lligadas and V. Percec, *Biomacromolecules*, 2019, **20**, 2135-2147.
2. C.-G. Wang, F. Hanindita and A. Goto, *ACS Macro Letters*, 2018, **7**, 263-268.
3. A. Moreno, D. Garcia, M. Galià, J. C. Ronda, V. Cádiz, G. Lligadas and V. Percec, *Biomacromolecules*, 2017, **18**, 3447-3456.
4. X.-R. Shen, Y.-J. Ding and J.-G. Gao, *Chemistry Letters*, 2017, **46**, 690-692.
5. N. Bensabeh, J. C. Ronda, M. Galià, V. Cádiz, G. Lligadas and V. Percec, *Biomacromolecules*, 2018, **19**, 1256-1268.
6. I. Zaborniak, M. Sroka and P. Chmielarz, *Polymer*, 2022, **254**, 125099.
7. M. Flejszar, P. Chmielarz, J. Smenda and K. Wolski, *Polymer*, 2021, **228**, 123905.
8. D. K. Schneiderman, J. M. Ting, A. A. Purchel, R. Miranda, M. V. Tirrell, T. M. Reineke and S. J. Rowan, *ACS Macro Letters*, 2018, **7**, 406-411.
9. M. Flejszar and P. Chmielarz, *Journal of Applied Polymer Science*, 2022, **n/a**, e53367.
10. C. Waldron, Q. Zhang, Z. Li, V. Nikolaou, G. Nurumbetov, J. Godfrey, R. McHale, G. Yilmaz, R. K. Randev, M. Girault, K. McEwan, D. M. Haddleton, M. Droesbeke, A. J. Haddleton, P. Wilson, A. Simula, J. Collins, D. J. Lloyd, J. A. Burns, C. Summers, C. Houben, A. Anastasaki, M. Li, C. R. Becer, J. K. Kiviaho and N. Risangud, *Polymer Chemistry*, 2014, **5**, 57-61.
11. Q. Zhang, P. Wilson, Z. Li, R. McHale, J. Godfrey, A. Anastasaki, C. Waldron and D. M. Haddleton, *Journal of the American Chemical Society*, 2013, **135**, 7355-7363.
12. A. Theodorou, E. Liarou, D. M. Haddleton, I. G. Stavrakaki, P. Skordalidis, R. Whitfield, A. Anastasaki and K. Velonia, *Nature Communications*, 2020, **11**, 1486.
13. C. Rodriguez-Emmenegger, E. Hasan, O. Pop-Georgievski, M. Houska, E. Brynda and A. B. Alles, *Macromolecular bioscience*, 2012, **12**, 525-532.
14. Y. Sun, S. Lathwal, Y. Wang, L. Fu, M. Olszewski, M. Fantin, A. Enciso, G. Szczepaniak, S. Das and K. Matyjaszewski, *ACS Macro Letters*, 2019, **8**, 603-609.
15. O. Rifaie-Graham, J. Pollard, S. Raccio, S. Balog, S. Rusch, M. A. Hernández-Castañeda, P.-Y. Mantel, H.-P. Beck and N. Bruns, *Nature Communications*, 2019, **10**, 1369.
16. J. Pollard, O. Rifaie-Graham, S. Raccio, A. Davey, S. Balog and N. Bruns, *Analytical Chemistry*, 2020, **92**, 1162-1170.
17. S. Averick, A. Simakova, S. Park, D. Konkolewicz, A. J. D. Magenau, R. A. Mehl and K. Matyjaszewski, *ACS Macro Letters*, 2012, **1**, 6-10.
18. G. Englezou, K. Kortsen, A. A. C. Pacheco, R. Cavanagh, J. C. Lentz, E. Krumins, C. Sanders-Velez, S. M. Howdle, A. J. Nedoma and V. Taresco, *Journal of Polymer Science*, 2020, **58**, 1571-1581.

19. P. Maximiano, J. P. Mendes, P. V. Mendonça, C. M. R. Abreu, T. Guliashvili, A. C. Serra and J. F. J. Coelho, *Journal of Polymer Science Part A: Polymer Chemistry*, 2015, **53**, 2722-2729.
20. V. A. Pereira, P. V. Mendonça, J. F. J. Coelho and A. C. Serra, *Polymer*, 2022, **242**, 124586.
21. Q. Zhang, Z. Li, P. Wilson and D. M. Haddleton, *Chemical Communications*, 2013, **49**, 6608-6610.