

Electronic Supporting Information

The Preparation of Graft Copolymers of Cellulose and Cellulose Derivatives Using ATRP Under Homogeneous Reaction Conditions

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List of abbreviations

AM: Acrylamide

AA: Acrylic acid

[AMIM]Cl: 1-Allyl-3-methylimidazolium chloride

AGU: β -D-anhydroglucopyranose

AFM: Atomic Force Microscopy

ATRP: Atom Transfer Radical Polymerisation

BA: n-Butyl acrylate

BMIMCl: 1-Butyl-3-methylimidazolium chloride

Bpy: 2,2'-bipyridine

CL: ϵ -Caprolactone

CM Cell: Carboxymethyl cellulose

Cell: Cellulose

CA: Cellulose acetate

CDA: Cellulose diacetate

CMA: Cholesteryl methacrylate

CRP: Controlled Radical Polymerisation

CMC: Critical Micelle Concentration

D_h: Hydrodynamic diameter

D_M : Dispersity
 DCM: Dichloromethane
 DEAEMA: 2-(Diethylamino)ethyl methacrylate
 DMAc: N,N-Dimethylacetamide
 DMA: N,N-Dimethylacrylamide
 DMAEMA: 2-(Dimethylamino)ethyl methacrylate
 DMAP: 4-Dimethylaminopyridine
 DMF: N,N-Dimethylformamide
 DMSO: Dimethyl sulfoxide
 DNpby: 4,4'-Di-5-nonyl-2,2'-bipyridine
 DLS: Dynamic Light Scattering
 DP: Degree of Polymerisation
 DS: Degree of Substitution
 DSC: Differential Scanning Calorimetry
 DEGMA: 2-(Hydroxyethoxy)ethyl methacrylate
 EC: Ethyl cellulose
 EMO: 3-Ethyl-3-methacryloyloxy-methyloxetane
 GPC: Gel Permeation Chromatography
 HS-GC: Headspace gas chromatography
 HDMA: Hexadecyl methacrylate
 HEC: Hydroxyethyl cellulose
 HEMA: 2-Hydroxyethyl methacrylate
 HMTETA: 1,1,4,7,10,10-Hexamethyltriethylenetetramine
 HPC: Hydroxypropyl cellulose
 IL: Ionic liquid
 LLA: L-lactide
 LCST: Lower Critical Solution Temperature
 Me₆TREN: Tris[2-(dimethylamino)ethyl]amine
 MMAzo: azobenzene-containing methacrylate
 MDEGMA: methyl diethylene glycol methacrylate

MMA: methylmethacrylate

NIPAAM: *N*-isopropylacrylamide

OEGMA: Oligo(ethylene glycol) methacrylate

PEG: Polyethylene glycol

PEGMA: Poly(ethylene glycol) methyl ether methacrylate

PMDETA: N,N,N',N',N''-pentamethyldiethylenetriamine

QDDMAEMA: Quaternized *N,N*-dimethylamino-2-ethyl methacrylate

RAFT: Reversible Addition Fragmentation Transfer

R_h: hydrodynamic radius

ROP: Ring Opening Polymerisation

St: Styrene

SLS: Static Light Scattering

T_g: Glass transition temperature

TEA: Triethylamine

TEM: Transmission Electron Microscopy

TG-DTA: Thermal Gravimetric-Differential Thermal Analysis

TMEDA: Tetramethylethylenediamine

4VP: 4-*N*-vinylpyridine

WAXD: Wide-Angle X-ray Diffraction

Table S1: Reaction conditions used to prepare cellulose ATRP macro-initiators

Ref.	Reactants	Catalyst	AGU:(Br/Cl)	Temperature (°C)	Time (h)	Solvent(s)	DS
40	Chloroacetyl chloride	pyridine	1:10	RT	10	DMAc/LiCl	2.1
41		/	1:5	50	5	BMIMCl	1.8
46		dimethylaminopyridine	..	50	5	DMAc/LiCl	..
51	2-Chloropropionyl chloride	dimethylaminopyridine	..	..	..	DMF	>1
49	2-Bromoisobutyryl bromide	pyridine	..	RT	~17	DMAc/LiCl	0.2
43		pyridine	1:20	RT	~17	DMAc	1
42		/	1:5	RT	8	AMIMCl/DMF	0.7
45	2-Bromopropionyl bromide	/	1:5	RT	8	AMIMCl/DMF	0.7
44		/	1:5	RT	10	AMIMCl/DMF	0.7
50	Methyl-2-bromopropionate	dimethylaminopyridine	1:30	25	..	THF	..

‘..’ = not reported; ‘/’ = no catalyst

Table S2: Summary of the reaction conditions for preparing graft-copolymers of cellulose

Ref.	Monomer	Initiator	Catalyst	Ligand	Solvent(s)	Temperature (°C)	Time (h)	Ratio [I]/[C]/[L]/[M]	Conversion (%)	$\bar{D}_M$	Graft Ratio
40	EMO	Cl-Cell	CuBr	PMDETA	DMF	130	21	1/1/3/9	..	..	10
		Cell-PMMA-Cl	CuCl	TMEDA	..	70	46	1/1/3/60	..	..	28
40	MMA	Cl-Cell	CuBr	TMEDA	DMF	130	20	1/1/3/60	..	..	7
		Cell-PEMO-Cl	CuCl	PMDETA	..	70	21	1/1/1/3/60	..	..	49
41		Cl-Cell	CuBr	bpy	BMIMCl		5	1/1/1/300	15	1.5	..
42		Br-Cell	CuCl		butanone		3	1/1/2/200	28	1.4	1493
44		Br-Cell	CuBr	PMDETA	DMF	60	3	1/1/1/200	38	1.6	1800
46		Cl-Cell	Cu(II)Br/ AsAc	TEMED	DMAc	50-70	3	1/0.1/1/100	13	1.4	553
49	DMA	Br-Cell	CuBr	bpy	DMSO	RT	7	1/2.9/1.3/90	50	1.5	2280
50		Br-Cell	CuBr	Me ₆ TREN	toluene	..	..	..1/1/(10 AA/20 DMA)	..	..	..
43	NIPAAM	Br-Cell	CuBr	PMDETA	DMF/H ₂ O	RT	12	1/4/4/200	17	2.3	14
51		Cl-Cell	CuCl	Me ₆ TREN	DMF/H ₂ O	80	48	1/1.2/1.2/100	79	1.4	..
45	DMAEMA	Br-Cell	CuBr	PMDETA	DMF	60	1	1/1/1/200	35	..	2670
42	St	Br-Cell	CuCl	bpy	dioxane	110	2	1/1/3/100	14	1.5	373

('..' = not reported) and Graft ratio = $(W_2 - W_1)/W_1 \times 100$ where W_2 and W_1 are weight of the graft-copolymers and macro-initiator respectively.

Table S3: Summary of the reaction conditions used to prepare ethyl cellulose ATRP macroinitiators

Ref.	DS _{EC}	Reactant	Catalyst	Time (h)	AGU:Br	DS _{Br-EC}
63	2.1	2-bromoisobutyryl bromide	triethylamine	10	1:5	(50 %)
53			pyridine	48	1:3	0.5
54					1:3	0.5
					1:0.2	0.04
54				24	..	0.04/0.25
56					1:1	0.04
					1:2	0.09
59			triethylamine	~17	1:3	0.5
60			..	..	..	0.02/0.2
62	2.3	2-bromopropionyl bromide	triethylamine	24	1:3	(23 %)
55	2.5	2-bromoisobutyryl bromide	pyridine	48	..	0.28/0.54
61			..	..	..	0.1/0.06/0.2

'..' = not reported

Table S4: Summary of reaction conditions for preparing graft-copolymers of EC

Ref.	Monomer	Solvent(s)	Ligand	Temperature (°C)	Ratio [I]/[C]/[L]	Catalyst (s)	Time (h)	DS _{Br-EC}	DP _{targeted}	Conversion (%)	<i>D</i> _M	Graft Ratio (%)
53,	MMA	toluene	PMDETA	70	1/0.5/1	CuBr	16	0.5	300	11.8	1.35	1291
55	St			110	1/0.5/1					10.8	1.35	1227
54	St			21.5	20		1.3			2272		
	St	Toluene	PMDETA	110	1/1/1	CuBr	10.5	0.04	6000	10	1.2	1115
57	tBA	toluene/ cyclohexan one	PMDETA	80	1/2/2		..	0.04	3750	6	1.16	518
					1/1/1	CuBr/ CuBr ₂	..	0.25	300	21	1.2	..
56	HEMA	methanol	bypyridine	40	1/1.5/2.6	CuBr/ CuBr ₂	12	0.09	510	13	1.15	401
					1/1/2	CuBr	10	0.04	1000	8.3	1.18	502
59	MMAzo	anisole	PMDETA	85	1/2/4	CuBr	20	0.5	25	18	..	325
									50	..	..	..
60	PEGMA	toluene	dNbpy	60	1/0.75/1.5	CuCl/ CuCl ₂	8	0.2	50	55.6	..	665

						CuCl	14	0.02	300	61.7	..	..
61	DEAEMA	DMF	bpy	20	1/1.5/2.5	CuBr	5	0.1	300	28	..	616
							4	0.2	450	24	..	..
							6.5	0.06	200	42	..	..
62	DMAEMA	THF	PMDETA	60	1/1/1	CuBr	30	23%	100	23	..	31
63	NIPAAM/ MMAzo	DMF/H ₂ O	Me ₆ TREN	80	1/1/1	CuCl	9	50%	50/1	..	..	..

‘..’ = not reported

Table S5: Summary of the R_h of micelles prepared from EC

Ref.	graft-copolymers	solvent	Concentration (mg/ml)	R_h^* (nm)
54	PSt ₆₀ -g-EC _{0.5}	acetone	0.02	200-300
57	PAA ₁₃ -g-EC _{0.25}	water	1	5-100
56	PHEMA ₁₃₁ -g-EC _{0.09}	water	0.01-0.05	66-73
	PHEMA ₁₀ -g-EC _{0.04}	water	0.01-0.05	79-83
60	P(PEGMA) ₂₇ -g-EC _{0.2}	water	1	73
	P(PEGMA) ₁₈₅ -g-EC _{0.02}	water	1	140
61	PDEAEMA ₍₃₅₋₈₅₎ -g-EC _{0.1}	acidic aqueous	0.5	140-200
	PDEAEMA ₉₀ -g-EC _(0.06-0.1)	acidic aqueous	0.5	200
62	PDMAEMA ₂₃ -g-PCL ₃₀ -g-EC	aqueous	0.5	36

* determined by DLS

Table S6: Reactions conditions for preparing macro-initiators of HPC

Ref.	Starting material	Reagents	Catalyst(s)	Solvent	Time (h)	DS
74	HPC	bromoisobutyryl bromide	..	DCM	5	0.14
72			..	DCM	6	0.14
75			Pyridine	THF	12	0.05
73			..	DCM	2.5	0.6
69			DMAP/Pyridine	DMF	5	2.04
68		bromoisobutyryl anhydride	DMAP/Pyridine	DMF	12	2.26
73						1.4
68		Br*	DMAP/TEA	DMF	12	0.88
70	HPC-PCL-I	bromoisobutyryl bromide	DMAP/TEA	THF	2	>1.1
71	HPC-PLLA-OH	bromopropionyl bromide	TEA	THF	48	1

*3(2-bromo2-methylpropanoylloxy02-((2-bromo-2-methylpropanoloxymethyl)2-methylpropanoic acid chloride; ‘..’ = not reported.

Table S7: Reaction conditions for the graft-copolymerisation onto HPC

Ref.	Monomer	Macro-initiator	Solvent(s)	Ligand	Temperature (°C)	Ratio [M]/[I]/[C]/[L]	Catalyst(s)	Time (h)	Conversion (%)	Graft Ratio (%)
68	MMA	Br _{2.26}	toluene	PMDETA	80	100/0.28/0.8/0.2/1	CuBr/CuBr ₂	19	39	4680
68		Br _{0.88} -G1	toluene	PMDETA	50	100/0.085/0.9/0.1/1	CuBr/CuBr ₂	2	18	..
69		Br _{2.04}	toluene	bpy	70	100/0.28/0.8/0.2/1	CuCl/CuBr ₂	19	25	3480
69	MMA/CMA	Br _{2.04}	toluene	bpy	70	100/0.28/0.8/0.2/1	CuCl/CuBr ₂	19	30	6288
68	HDMA	Br _{2.26}	toluene	PMDETA	50-80	..	CuBr/CuBr ₂	1-2	gelled	..
68		Br _{0.88} -G1	toluene	PMDETA	70	100/0.19/0.8/0.2/1	CuBr/CuBr ₂	20	23	..
68	t-BA	Br _{2.26} -PMMA	toluene	PMDETA	70	100/0.1/0.8/0.2/1	CuBr/CuBr ₂	22	3.5	210
70		Br _{>1.1} -PCL	toluene	PMDETA	70	..	CuBr/CuBr ₂	14	32	1920
71		Br ₁	/	PMDETA	100	152/1/1/1	CuBr	0,5	35	475
74	DMAEMA	Br _{0.14}	isopropanol/ H ₂ O	HMTETA	RT	60/1/1/1.2	CuBr	8	62	289
72	NIPAAM	Br _{0.14}	dioxane	HMTETA	RT	100/1/1.5	CuBr	24	64	320
75	4VP	Br _{0.05}	isopropanol	Me ₆ TREN	30	100/1/1	CuCl	6	35	55

73	DEGMA	Br _{1.4}	anisole	Bpy	40	425/1	CuBr ₂ / AcAsc	..	20	2368
73	DEGMA	Br _{0.6}	MeOH	bpy	40	850/1/./..		4	21	2487
73	OEGMA	Br _{0.6}	MeOH	bpy	40	850/1/./..		4	28	5712
73	OEGMA52- co- DEGMA48	Br _{0.6}	MeOH	bpy	40	850/1/./..		4	35	..

‘..’ = not reported

Table S8: Hydrodynamic radii (R_h) of the micelles formed with graft-copolymers of HPC

Ref.	Graft-copolymers	Solvent(s)	R_h^*
71	PAA-PLLA-g-HPC	EtOH/H ₂ O	64
70	PtBA-PCL-g-HPC	H ₂ O	43
68	PMMA-g-HPC _{2.26}	THF	96
73	PDEGMA-g-HPC _{0.6}	H ₂ O	120
70	PAA-PCL-g-HPC _{>1.1}	H ₂ O	129
73	POEGMA-g-HPC _{0.6}	H ₂ O	150
68	PHDMA-g-GI-HPC _{0.88}	THF	183
75	P4VP ₃₅ -g-HPC _{0.05}	H ₂ O	190
68	PMMA-g-GI-HPC _{0.88}	THF	195
73	P(OEGMA ₅₂ -co-DEGMA ₄₈)-g-HPC _{0.6}	H ₂ O	200
73	PDEGMA-g-HPC _{1.4}	H ₂ O	250
70	cross linked PAA-PCL-g-HPC _{>1.1}	H ₂ O	235.3
68	PtBA-PMMA-g-HPC _{2.26}	THF	280
69	P(MMA-rand-CMA)-g-HPC _{2.04}	H ₂ O	570

*determined using DLS

Table S9: Reaction conditions for preparing macro-initiators of derivatives

Ref.	Derivative	Reagents	Ratio AGU:Br	Catalyst(s)	Solvent(s)	DS
78	CDA	bromoisobutyryl bromide	01:0.5	pyridine	THF	0.43
79, 80			1/(0.3 or 3.1)	TEA/DMAP	dioxane	0.12- 0.52
79		dichloroacetyl chloride	1/(1 or 4)	TEA/DMAP	acetone	0.10- 0.41
81	CA	bromoisobutyryl bromide	1/0.08	TEA	THF	0.01
82, 83	HEC	bromoisobutyryl bromide	..	TEA/DMAP	DMF/THF	..

‘..’ = not reported

Table S10: Reaction conditions for synthesising graft-copolymers of other cellulose derivatives

	Monomer	Solvent	Ligand	Catalyst(s)	Macro-initiator	Ratio [M]/[I]/[C]/[L]	Temp. (°C)	Time (h)	Conversion (%)	Graft Ratio (%)	Ref.
CDA	MMA	dioxane	PMDETA	CuBr	Br _{0.43}	300/1/0.5/1	70	8	4	177	78
			bpy	CuCl/CuCl ₂	Cl _{0.41}	1240/1/(2/1)/4	75	6.5-18	5-10	..	79
			HMDETA		Cl _{0.1}	380/1/(1/0.5)/1	90	1.5	18	..	79
						710/1/(2/1)/2		2.5	21	..	79
					Br _{0.5} -PCL ₅₀	500/1/(1/0.5)/1	70	7	6	50	80
			Br _{0.12/0.52}		(230-680)/1/(1/0.5)/1	110	9-12	9-14	..	79	
			Br _{0.5} -PCL ₅₀	500/1/(1/0.5)/1	110	8	7	..	80		
	St										
	BuA	acetone	PMDETA	CuCl/CuCl ₂	Br _{0.12}	410/1/(1/1)/2	70	5	25	..	79
					Br _{0.52}	440/1/(1/3)/2	60	8.5	15	..	79
				CuCl	Br _{0.12} -PSt ₂₅	720/1/1/2	60	20	5	..	79
					Cl _{0.1} -PMMA ₆₉	580/1/1/2	60	27	10	..	79
Br _{0.5} -PCL ₈₉		750/1/1/2			70	8	10	..	80		
	anisole										

CA	MDEGMA	cyclopentanone	PMDETA	CuCl	Br _{0.06}	100/1/1/2	40	2.5	16	..	81
					Br _{0.01}	425/1/3/7		7	19	60.8	81
HEC	AM	DMF/THF	Me6[14]aneN4	CuBr/CuBr ₂	Br	200/1/(1/0.1)/3	30	72	40.5	..	82
	DMA	DMF/toluene				100/1/(1/0.1)/3		6	61.5	..	83