Efficient polymerization and post-modification of *N*-substituted eight-membered cyclic carbonates containing allyl groups

Alexander Y. Yuen^a, Amaury Bossion^{a,b}, Antonio Veloso^a, David Mecerreyes^{a,c}, James L. Hedrick^d, Andrew P. Dove^e and Haritz Sardon^{a*}

^aPOLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-San Sebastian, Spain.

^bLaboratoire de Chimie des Polymères Organiques (LCPO), UMR 5629-CNRS-Université de Bordeaux – Institut National Polytechnique de Bordeaux, 16 Avenue Pey Berland, 33607 Pessac, France

^cIkerbasque, Basque Foundation for Science, E-48011 Bilbao, Spain.

^dIBMAlmaden Research Center, 650 Harry Road, San Jose, CA 95120, USA.

eSchool of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK, B15 2TT

E-mail: haritz.sardon@ehu.eus



Figure 1. ¹H NMR of diethanolamine functionalized with allyl chloroformate in d₆-DMSO.



Figure 2. ¹³C NMR of diethanolamine functionalized with allyl chloroformatein d₆-DMSO.



Figure 3. ¹H NMR of diethanolamine functionalized with allyl chloroformate in CDCl₃.



Figure 4. ¹H NMR of diethanolamine functionalized with allyl chloride in d₆-DMSO.



Figure 5. ¹³C NMR of diethanolamine functionalized with allyl chloride in d_6 -DMSO.



Figure 6. ¹H NMR of **8-ACfm** in d₆-DMSO.



Figure 7. ¹³C NMR of **8-ACfm** in d_6 -DMSO.



Figure 8. ¹H NMR of **8-ACI** in d₆-DMSO.



Figure 9. ¹³C NMR of **8-ACI** in d_6 -DMSO.



Figure 10. ¹H NMR of **Polymer 2** in CDCl₃.



Figure 11. ¹³CNMR of **Polymer 2** in CDCl₃.



Figure 12. ¹H NMR of **Polymer 2** ind₆-DMSO.



Figure 13. ¹³C NMR of **Polymer 2** ind₆-DMSO.



Figure 14. ¹H NMR of **Polymer 6** in d₆-DMSOafter two days of reaction.



Figure 15. ¹H NMR of **Polymer 6** in CDCl₃.



Figure 16.¹H NMR of **Polymer 2a** in CDCl₃.



Figure 17.¹³C NMR of **Polymer 2a** in CDCl₃.



Figure 18.¹H NMR of **Polymer 2b** in CDCl₃.



Figure 19.¹³C NMR of **Polymer 2b** in CDCl₃.



Figure 20.¹H NMR of **Polymer 2c** in d₆-DMSO.



Figure 21.¹³C NMR of **Polymer 2c** in d₆-DMSO.



Figure 22.¹H NMR of **Polymer 2d** in CDCl₃.



Figure 23.¹³C NMR of **Polymer 2d** in CDCl₃.



Figure 24.¹H NMR of **Polymer 5** in CDCl₃.



Figure 25.¹H NMR of **Polymer 7**in CDCl₃.



Figure 26.¹H NMR of **Polymer 7a** in CDCl₃.



Figure 27. FTIR-ATR of diethanolamine functionalized with allyl chloride.



Figure 28. FTIR-ATR of diethanolamine functionalized with allyl chloroformate.



Figure 29.FTIR-ATR of 8-ACI.



Figure 30.FTIR-ATR of 8-ACfm.



Figure 31.FTIR-ATR of Polymer 6.



Figure 32.FTIR-ATR of **Polymer 2**.



Figure 33.FTIR-ATR of **Polymer 2a**.



Figure 34.FTIR-ATR of **Polymer 2b**.



Figure 35.FTIR-ATR of **Polymer 2c**.



Figure 36.FTIR-ATR of **Polymer 2d**.



Figure 37.FTIR-ATR of **Polymer 5**.



Figure 38.FTIR-ATR of Polymer 9.



Figure 39.FTIR-ATR of **Polymer 9a**.



Figure 40. MALDI-ToF of **Polymer 2**, and a mixture of cyclic (**●**) and linear (**●**) polycarbonates were detected.

Polymer	Initiator (I)	Monomer (M)	Catalyst (C)	[I] ₀ :[M] ₀ :[C]	Time	% Conv. ^a	M _{n,NMR} (kDa) ^a	M _{n,SEC} (kDa) ^b	$\mathbf{\hat{B}}_{\text{SEC}}^{\ b}$
1	BnOH	8-ACfm	DBU	1:10:1	1 h	≥97	2.4	1.1	1.2
2	BnOH	8-ACfm	DBU	1:50:5	1 h	\geq 97	8.7	6.1	1.1
3	BnOH	8-ACfm	DBU	1:100:10	1 h	\geq 97	15.1	6.0	1.2
4	BnOH	8-ACfm	DBU	1:200:20	1 h	≥97	37.3	7.0	1.2
5	PEG _{8k}	8-ACfm	DBU	1:50:5	1 h	≥ 97	18.7	14.4	1.2
6	BnOH	8-ACl	DBU	1:50:5	2 w	81	6.4	2.6	1.3

Table S1. Polymerization conditions and SEC results from ROP of 8-ACfm and 8-ACl

All reactions were conducted in DCM at room temperature inside a N₂ filled glovebox. ^aConversion was determined by ¹H NMR spectroscopy. ^bMolecular weight (M_n) and polydispersity (Θ) were characterized using size exclusion chromatography SEC in THF, the reported numbers are in reference to polystyrene standards.

Table S2. Post-polymerization radical thiol-ene functionalization of polycarbonates.

Polymer	Thiol	Yield of modification	M _{n,SEC} (kDa)	\mathbf{D}_{SEC}
2	(none)	-	6.1	1.1
2a	1-butanethiol	95%	8.3	1.2
2b	1-hexanethiol	92%	13.0	1.1
2c	3-mercaptopropionic acid	≥97%	7.8	1.1
2d	2-mercaptoethanol	≥97%	6.5	1.2

Table S3. Co	polymerization	of with 8-ACfm	to access functiona	al copolymers

Polymer	Init. (I)	Monomer (M1)	Monomer (M2)	Catalyst (C)	$[I]_0:[M_1]_0:[M_2]_0:[C]$	Time	Conv. % (M1)	Conv. % (M2)	M _{n,SEC} (kDa)	$\mathbf{D}_{ ext{sec}}$
9	BnOH	8-ACfm	TMC	DBU	1:25:25:5	1 d	≥97	93	5.1	1.3

Table S4. Post-polymerization radical thiol-ene functionalization with 1-butanethiol of copolymers

Polymer	Thiol	M _{n,SEC} (kDa)	$\mathbf{\tilde{D}}_{\mathrm{SEC}}$	
9	(none)	5.1	1.3	
9a	1-butanethiol	7.2	1.4	