Supporting Information

Switchable copolymerization of mixed monomers catalyzed by imidazolium ionic liquids

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1. Experimental sections

Chemicals

Unless otherwise stated, all chemicals are used without further purification. Propylene oxide (PO), cyclohexene oxide (CHO), allyl glycidyl ether (AGE), phthalic anhydride (PA), norbornene dianhydride (NA), Succinic anhydride (SA), glutaric anhydride (GA), Tetrahydrofuran (THF). Styrene oxide (SO) were purchased fromAladdin. ε-caprolactone(ε-CL), L-Lactide (LA), delta-Valerolactone(δ-VL), 1ethyl-3-methylimidazole chlorine (EMIMCl), 1-ethyl-3-methylimidazole bromide 1-ethyl-3-methylimidazole iodine (EMIMBr), (EMIMI), 1-ethyl-3methylimidazoletetrafluoroborate (EMIMBF₄),1-ethyl-3-methylimidazole hexafluorophosphate (EMIMPF₆) were purchased from Energy Chemical. PO, CHO, AGE, SO, 1-Methylimidazole, THF and Toluene were dried over CaH₂ for 48 h, distilled in N2 or vacuum, and stored under nitrogen atmosphere. PA were used without purification. All manipulations were performed using a standard Schlenk technique unless otherwise mentioned.

Methods

¹H NMR, ¹³C NMR and DOSY NMR spectra were recorded on a Bruker Avance III spectrometer at room temperature in chloroform-d1 or Dimethyl sulfoxide-d6, and chemical shifts were referenced to an internal standard. DOSY NMR analyses were performed at a steady temperature of 25 °C with at least 16 gradient increments using the ledbpgp2s sequence. Gel permeation chromatography (GPC) analyses were carried out at 40 °C and a flow rate of 1.0 mL/min, with THF as the eluent on an Agilent PL-GPC 50 instrument coupled with a refractive index (RI) detector with respect to polystyrene (PS) standards. The columns included a Plgel guard 50×7.5 mm column, a PLgel mixed-B 300×7.5 mm column and a PLgel mixed-C 300×7.5 mm column. Samples being tested were filtered through a 0.22 µm PTFE filter. Ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer. Samples were dissolved in THF (10 mg mL⁻¹) and mixed with a solution of sodium trifluoroacetate (NaTFA) in THF (10 mg mL⁻¹) in a volume ratio of 5:1. This solution was then mixed with a THF solution of matrix (2, 5-dihdroxybenzoic acid, 20 mg mL⁻¹) in a volume ratio of 1:10. Then, 0.4 μ L of the final solution was spotted on the target plate (dried-droplet method). The reflective positive ion mode was used to acquire the mass spectra of the samples. Calibration was done externally with poly(methyl methacrylate) standards using the nearest neighbor positions.

ROAC

Poly(phthalic anhydride-alt-propylene oxide), PPAPO. A typical procedure for PPAPO (Table 1) is given as follows: the appropriate amount of EMIMCI (0.52 mmol, 1 equiv.) and PA (26 mmol, 50 equiv.) were added in an oven-dried tube equipped with a magnetic stir, vacuum for 30 minutes, then add PO (67 mmol, 100 equiv.) and THF (5 mL). The tube was left to react in a silicone oil at 100 °C for 1.4 hours and opened to air to quench the reaction. During polymerization, a crude aliquot was time-regularly withdrawn from the system and monitored by ¹H NMR spectroscopy and GPC to determine monomer conversion and molar mass. After the defined time, the reaction mixture was diluted with approximately 5 mL Trichloromethane and dropwise precipitated into 100 mL of methanol acidified by hydrochloric acid with vigorous stirring, after which the methanol was filtrated or poured out. The resulting polymers were dried under vacuum at 60 °C.

ROP

Poly(ε -caprolactone), PCL. A typical procedure for PCL(Table S4) is given as follows: the appropriate amount of EMIMCl (0.52 mmol, 1 equiv.) were added in an oven-dried tube equipped with a magnetic stir, vacuum for 30 minutes, then add CL (34 mmol, 50 equiv.), PO (67 mmol, 100 equiv.) and THF (5 mL). The tube was left to react in a silicone oil at 100 °C for 9 hours and opened to air to quench the reaction. During polymerization, a crude aliquot was time-regularly withdrawn from the system and monitored by ¹H NMR spectroscopy and GPC to determine monomer conversion and molar mass. After the defined time, the reaction mixture was diluted with approximately 5 mL Trichloromethane and dropwise precipitated into 100 mL of methanol acidified by hydrochloric acid with vigorous stirring, after which the methanol was filtrated or poured out. The resulting polymers were dried under vacuum at 60 °C.

Block copolymer Synthesis in a one-step procedure

A typical polymerization procedure was as follows: the appropriate amount of EMIMC1 (0.52 mmol, 1 equiv.), PA (26 mmol, 50 equiv.) and CL (34 mmol, 50 equiv.) were added in an oven-dried tube equipped with a magnetic stir, vacuum for 30 minutes, then add PO (67 mmol, 100 equiv.) and THF (5 mL). The tube was left to react in a silicone oil at 100 °C for 9 hours and opened to air to quench the reaction. During polymerization, a crude aliquot was time-regularly withdrawn from the system and monitored by ¹H NMR spectroscopy and GPC to determine monomer conversion and molar mass. After the defined time, the reaction mixture was diluted with approximately 5 mL Trichloromethane and dropwise precipitated into 100 mL of methanol acidified by hydrochloric acid with vigorous stirring, after which the methanol was filtrated or poured out. The resulting polymers were dried under vacuum at 60 °C. All analyses and further chemical modification were performed on crude samples.

2. The alternating copolymerization of PA and PO using EMIMCI



Figure S1. The ¹H NMR spectra in situ of crude aliquots withdrawn from the reaction system for monitoring the conversion of PA and the formation of PPAPO.



Figure S2. The ¹H NMR spectrum of the resultant PPAPO isolated from the mixture by precipitation. (Table 1, entry 5)



Figure S3. The GPC trace of the resultant PPAPO.



Figure S4. The fittings of zero-order kinetic plots and first-order kinetic plots with respect to PA suggesting that the insertion of PA complies with zero-order kinetics.

2.1 Copolymerization of PO and PA with different feed ratios

Entry	Cata./PA/PO	Time (h)	Conv.(%) ^b	Ether (%) °				
1	1/25/25	3	50	<1				
2	1/25/50	3	91	<1				
3	1/50/100	1.4	>99	<1				

Table S1. The ROAC of PA and PO with different feed ratios ^a

^a The copolymerization reactions were conducted in 5 mL THF at 100 °C. ^b The conversion of PA was determined by ¹H NMR spectroscopy. ^c The content of ether was determined by ¹H NMR spectroscopy.



Figure S5. ¹H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of PA and the formation of PPAPO using EMIMCl as catalyst.

2.2 Copolymerization of PO and PA by ionic liquids with different anions

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Entry	Cata.	Time(h)	Conv.(%) ^b	Ether (%) ^c
1	EMIMCl	1.4	>99	<1
2	EMIMBr	1.6	>99	<1
3	EMIMI	1.6	83	<1
4	EMIMPF ₆	1.6	75	<1
5	EMIMBF ₄	1.6	11	<1

Table S2. The ROAC of PA and PO by ionic liquids different anions^a

^a The copolymerization reactions were conducted in 5 mL THF at 100 °C. ^b The conversion of PA was determined by ¹H NMR spectroscopy. ^c The content of ether was determined by ¹H NMR spectroscopy.



Figure S6. ¹H NMR spectra of the aliquots withdrawn from the copolymerization of PA and PO using EMIMBr as catalyst (Table S2, entry 2).



Figure S7. ¹H NMR spectra of the aliquots withdrawn from the copolymerization of PA and PO using EMIMI as catalyst (Table S2, entry 3).



Figure S8. ¹H NMR spectra of the aliquots withdrawn from the copolymerization of PA and PO using $[EMIM^+][PF_6^-]$ as catalyst (Table S2, entry 4).



Figure S9. ¹H NMR spectra of the aliquots withdrawn from the copolymerization of PA and PO using [EMIM⁺][BF₄⁻] as catalyst (Table S2, entry 5).



Figure S10. The possible reaction mechanism of PA and PO copolymerization catalyzed by EMIMCl.

3. The polymerization of CL catalyzed by EMIMCl



Figure S11. The ¹H NMR spectra in situ of crude aliquots withdrawn from the reaction system for monitoring the conversion of CL and the formation of PCL.



Figure S12. The ¹H NMR spectrum of the resultant PCL isolated from the mixture by precipitation(Table 2, entry 5).



Figure S13. The GPC trace of the resultant PCL.



Figure S14. The fittings of zero-order kinetic plots and first-order kinetic plots with respect to CL suggesting that the insertion of CL complies with first-order kinetics.

3.1 Polymerization of CL with different feed ratio of PO

Entry	Cata./PO/CL	Time (h)	Conv.(%) ^b	Ether (%) °
1	1/0/50	5	<1	<1
2	1/50/50	5	33	<1
3	1/100/50	5	88	<1
4	1/150/50	5	47	<1

Table S3. The ROP of CL with different feed ratio of PO^a

^a The copolymerization reactions were conducted in 5 mL THF at 100 °C. ^b The conversion of CL was determined by ¹H NMR spectroscopy. ^c The content of ether was determined by ¹H NMR spectroscopy



Figure S15. The ¹H NMR spectra in situ of crude aliquots withdrawn from the reaction system for monitoring the conversion of CLand the formation of PCL.



Figure S16 The possible reaction mechanism of CL copolymerization catalyzed by EMIMCl.

3.2 ROP of CL using imidazolium ionic liquids with different anions

Entry	Cata.	Time (h)	Conv.(%)	Ether (%) °
1	EMIMC1	9	>99	<1
2	EMIMBr	9	5	<1
3	EMIMI	9	0	<1
4	$[EMIM^+][PF_6^-]$	9	0	<1
5	$[EMIM^+][BF_4^-]$	9	0	<1

Table S4. ROP of CL using imidazolium ionic liquids with different anions

^a The copolymerization reactions were conducted in 5 mL THF at 100 °C.^b The conversion of PA was determined by ¹H NMR spectroscopy. ^cThe content of ether was determined by ¹H NMR spectroscopy



Figure S17. ¹H NMR spectra of the aliquots withdrawn from the polymerization of CL using EMIMBr as catalyst (Table S4, entry 2).



Figure S18. ¹H NMR spectra of the aliquots withdrawn from the terpolymerization of mixed PCL and EMIMI as catalyst (Table S4, entry 3).



Figure S19. ¹H NMR spectra of the aliquots withdrawn from the terpolymerization of mixed PCL and $[EMIM^+][PF_6^-]$ as catalyst (Table S4, entry 4).



Figure S20. ¹H NMR spectra of the aliquots withdrawn from the terpolymerization of mixed PCL and [EMIM⁺][BF₄⁻]as catalyst (Table S4, entry 5).

4. Terpolymerization of PO, PA and CL



Figure S21. The conversion of PA and CL in copolymerization catalyzed by EMIMCl.

4.1. Characterization of PPAPO-b-PCL



Figure S22. The ¹H NMR spectrum of the resultant PPAPO-b-PCL isolated from the mixture by precipitation (Table 3, entry 7).



Figure S23. The ¹³C NMR spectrum of the resultant PPAPO-b-PCL isolated from the mixture by precipitation (Table 3, entry 7).

4.2 Transesterification with DBU



Figure S24. The comparison about ¹H NMR spectra of the resultant PPAPO-b-PCL and random copolymer by transesterification using DBU.

entry	Time (h)	Conv	Ethor d	
	Time (ii)	PA ^b	CL °	
1	2	-	10	<1
2	2.1	42	10	<1
3	2.2	51	10	<1
4	2.3	67	10	<1
5	2.5	>99	10	<1
7	5.0	>99	49	<1
8	7.0	>99	70	<1
9	9.0	>99	95	<1

Table S5. The CL polymerization in the presence of PO and subsequent addition of PA in this system catalyzed by EMIMCl^a.

^a The copolymerization reactions were conducted in 5 mL THF at 100°C, [IL]:[PO]:[CL]=1:100:50, another 8 mmol PA and 8 mL THF was added into the mixtures when the reaction was extended to 2 h.. ^{b, c, d} The conversion of PA and CL and the content of ether was determined by ¹H NMR spectroscopy.



Figure S25. The ¹H NMR spectra of crude aliquots withdrawn from polymerization system for monitoring the conversion of PA and CL.

4.3 Electrostatic potential (ESP) analysis results



Figure S26. The ESP of EMIM⁺.



Figure S27. The ESP of alkoxide anion from PO.



Figure S28. The ESP of carboxylic acid anion from PA.



Figure S29. The ESP of alkoxide anion from CL.

entry	Cata.	ratio ^b	Time (h)	Conv.(%)	
				PA ^c	CL d
1	EMIMBr	1:50:100:50	13	100	30
2	EMIMI	1:50:100:50	13	100	20
3	$[EMIM^+][PF_6^-]$	1:50:100:50	13	46	-
4	[EMIM ⁺][BF ₄ ⁻]	1:50:100:50	13	100	11

Table S6 The terpolymerization of PA, PO and CL catalyzed via different anionic ionic liquids^a.

5. Terpolymerization of PO, PA and CL by Different anions

^a The copolymerization reactions were conducted in 5 mL THF at 100 °C. ^b The ratio is catalyst to monomer. ^c The conversion of PA was determined by ¹H NMR spectroscopy. ^d The conversion of CL was determined by ¹H NMR spectroscopy.

5.1 EMIMBr



Figure S30. ¹H NMR spectra of the aliquots withdrawn from mixed monomers of PA, PO and CL using EMIMBr catalyst (Table S6, entry 1).

5.2 EMIMI



Figure S31. ¹H NMR spectra of the aliquots withdrawn from mixed monomers of PA, PO and CL using EMIMI catalyst (Table S6, entry 2).

5.3 [EMIM⁺][PF₆⁻]



Figure S32. ¹H NMR spectra of the aliquots withdrawn from mixed monomers of PA, PO and CL using [EMIM⁺][PF₆⁻] catalyst (Table S6, entry 3).

5.4 [EMIM⁺][BF₄⁻]



Figure S33. ¹H NMR spectra of the aliquots withdrawn from mixed monomers of PA, PO and CL using [EMIM⁺][BF₄⁻] catalyst (Table S6, entry 4).

6. Terpolymerizations of PA, CL and various epoxides

In this section, polymerization containing mixed feedstocks of epoxides, PA and CL was performed in bulk at 100 °C. The ¹H NMR spectra and GPC traces of the time-regular aliquots uncovered the route for various catalytic cycles. The presence of PA in such system switched the ROP of CL off, and it was switched on only after the full consumption of PA. In order to characterize the polymer composition, a series of measurement including ¹H NMR, ¹³C NMR, and DOSY NMR were applied, attesting the formation of block copolymers.

Entry	Epoxide	Time (h)	Conv. (%)		Ether ^d	M_n (kg/mol) ^e	Đ e
			PA ^b	CL ^c			
1	SO	12	>99	43	<1	8.6	1.8
2	СНО	12	>99	39	<1	8.5	1.5
3	AGE	12	>99	73	<1	9.0	1.9

Table S7 The terpolymerization of PA, CL and epoxides catalyzed by EMIMCL^a.

^a The copolymerization reactions were conducted in 5 mL THF at 100 °C, [IL]:[PA]:[Epoxide]:[CL]= 1:50:100:50. ^b The conversion of PA was determined by ¹H NMR spectroscopy. ^c The conversion of LA was determined by ¹H NMR spectroscopy. ^d The content of ether was determined by ¹H NMR spectroscopy. ^e M_n and D were determined by GPC analysis in DMF calibrated with polystyrene standards.

6.1. SO



Figure S34. The ¹H NMR spectrum of the resultant PPASO-b-PCL isolated from the mixture by precipitation (Table S7, entry 1).



Figure S35. The ¹³C NMR spectrum of the resultant PPASO-b-PCL isolated from the mixture by precipitation (Table S7, entry 1).



Figure S36. The GPC trace of the resultant PPASO-b-PCL (Table S7, entry 1).



Figure S37. The DOSY NMR spectrum of the resultant PPASO-b-PCL isolated from the mixture by precipitation (Table S7, entry 1).

6.2. CHO



Figure S38. The ¹H NMR spectrum of the resultant PPACHO-b-PCL isolated from the mixture by precipitation (Table S7, entry 2).



Figure S39. The ¹³C NMR spectrum of the resultant PPACHO-b-PCL isolated from the mixture by precipitation (Table S7, entry 2).



Figure S40. The GPC trace of the resultant PPACHO-b-PCL (Table S7, entry 2).



Figure S41. The DOSY NMR spectrum of the resultant PPACHO-b-PCL isolated from the mixture by precipitation (Table S7, entry 2).

6.3. AGE



Figure S42. The ¹H NMR spectrum of the resultant PPAAGE-b-PCL isolated from the mixture by precipitation (Table S7, entry 3).



Figure S43. The ¹³C NMR spectrum of the resultant PPAAGE-b-PCL isolated from the mixture by precipitation (Table S7, entry 3).



Figure S44. The GPC trace of the resultant PPAAGE-b-PCL (Table S7, entry 3).



Figure S45. The DOSY NMR spectrum of the resultant PPAAGE-b-PCL isolated from the mixture by precipitation (Table S7, entry 3).

7. Terpolymerization of PO, CL and different anhydrides

In this section, polymerization containing mixed feedstocks of different anhydrides, PO and CL was performed in bulk at 100 °C. The ¹H NMR spectra and GPC traces of the time-regular aliquots uncovered the route for various catalytic cycles. The presence of anhydrides in such system switched the ROP of CL off, and it was switched on only after the full consumption of anhydrides. In order to characterize the polymer composition, a series of measurement including ¹H NMR, ¹³C NMR, and DOSY NMR were applied, attesting the formation of block copolymers.

Entry	Anhydride	Time (h)	Conv. (%) ^b		Ether ^c	M_n (kg/mol) ^d	\mathcal{D}^{d}
			Anhydride	CL			
1	NA	12	>99	>99	<1	18.6	1.25
2	SA	12	>99	46	<1	16.8	1.26
3	GA	12	>99	79	<1	21.2	1.24

Table S8 The terpolymerization of PO, CL and anhydride monomer catalyzed by EMIMCl ^a

^a The copolymerization reactions were conducted in 2.5 mL THF at 120°C, [IL]:[Anhydride monomer]:[PO]:[CL]= 1:50:100:50. ^{b,c}The conversion of anhydride monomer, CL and ether was determined by ¹H NMR spectroscopy. ^d M_n and D were determined by GPC analysis in DMF calibrated with polystyrene standards.

7.1. NA



Figure S46. The ¹H NMR spectrum of the resultant PNAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 1).



Figure S47. The ¹³C NMR spectrum of the resultant PNAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 1).



Figure S48. The GPC trace of the resultant PNAPO-b-PCL (Table S8, entry 1).



Figure S49. The DOSY NMR spectrum of the resultant PNAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 1).

7.2. SA



Figure S50. The ¹H NMR spectrum of the resultant PSAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 2).



Figure S51. The ¹³C NMR spectrum of the resultant PSAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 2).



Figure S52. The GPC trace of the resultant PSAPO-b-PCL (Table S8, entry 2).



Figure S53. The DOSY NMR spectrum of the resultant PSAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 2).

7.3. GA



Figure S54. The ¹H NMR spectrum of the resultant PGAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 3).



Figure S55. The ¹³C NMR spectrum of the resultant PGAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 3).



Figure S56. The GPC trace of the resultant PGAPO-b-PCL (Table S8, entry 3).



Figure S57. The DOSY NMR spectrum of the resultant PGAPO-b-PCL isolated from the mixture by precipitation (Table S8, entry 3).

8. Terpolymerization of PA, PO and various Lactones

In this section, polymerization containing mixed feedstocks of various Lactones, PA and PO was performed in bulk at 100 °C. The ¹H NMR spectra and GPC traces of the time-regular aliquots uncovered the route for various catalytic cycles. The presence of PA in such system switched the ROP of CL off, and it was switched on only after the full consumption of PA. In order to characterize the polymer composition, a series of measurement including ¹H NMR, ¹³C NMR, and DOSY NMR were applied, attesting the formation of block copolymers.

Entry	Lactones	Time (h)	Conv. (%)		Ether ^d	M_n^{e} (kg/mol)	Đe
			PA ^b	Lactones ^c			
1	LA	7	100	100	<1	9.1	1.80
2	VL	8	100	100	<1	9.9	1.90

Table S9 The terpolymerization of PA, PO and Lactones catalyzed by EMIMCL^a.

^a The copolymerization reactions were conducted in 5 mL THF at 100 °C, [IL]:[PA]:[PO]:[Lactones]= 1:50:100:50. ^b The conversion of PA was determined by ¹H NMR spectroscopy. ^c The conversion of Lactones monomer was determined by ¹H NMR spectroscopy. ^d The content of ether was determined by ¹H NMR spectroscopy. ^e M_n and D were determined by GPC analysis in DMF calibrated with polystyrene standards.

8.1. LA



Figure S58. The ¹H NMR spectrum of the resultant PPAAGE-b-PLA isolated from the mixture by precipitation (Table S9, entry 1).



Figure S59. The ¹³C NMR spectrum of the resultant PPAPO-b-PLA isolated from the mixture by precipitation (Table S9, entry 1).



Figure S60. The GPC trace of the resultant PPAPO-b-PLA (Table S9, entry 1).



Figure S61. The DOSY NMR spectrum of the resultant PPAPO-b-PLA isolated from the mixture by precipitation (Table S9, entry 1).

8.2.VL



Figure S62. The ¹H NMR spectrum of the resultant PPAPO-b-PVL isolated from the mixture by precipitation (Table S9, entry 2).



Figure S63. The ¹³C NMR spectrum of the resultant PPAPO-b-PVL isolated from the mixture by precipitation . (Table S9, entry 2)



Figure S64. The GPC trace of the resultant PPAPO-b-PVL (Table S9, entry 2).



Figure S65. The DOSY NMR spectrum of the resultant PPAPO-b-PVL isolated from the mixture by precipitation (Table S9, entry 2).