Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Mechanistic Investigation of Cyclic Ketene Acetal Radical Ring-Opening Homo- and Co-Polymerization and Preparation of PEO Graft Copolymers With Tunable Composition

Yifeng Du,[1,‡,*] Yuhui Du,[2,‡] Stefano Lazzari,[3] Tom Reimers,[2,†] Rupert Konradi,[4] Thomas W. Holcombe,[1] E. Bryan Coughlin[2,*]

[1]BASF Advanced Chemicals Co., Ltd., Shanghai, 200137, China

[2]Department of Polymer Science & Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, 01003, USA

[3]BASF SE, Digitalization, Automation & Innovation Management, Ludwigshafen, 67056, Germany

[4]BASF Corporation, Cambridge, Massachusetts, 02138, USA

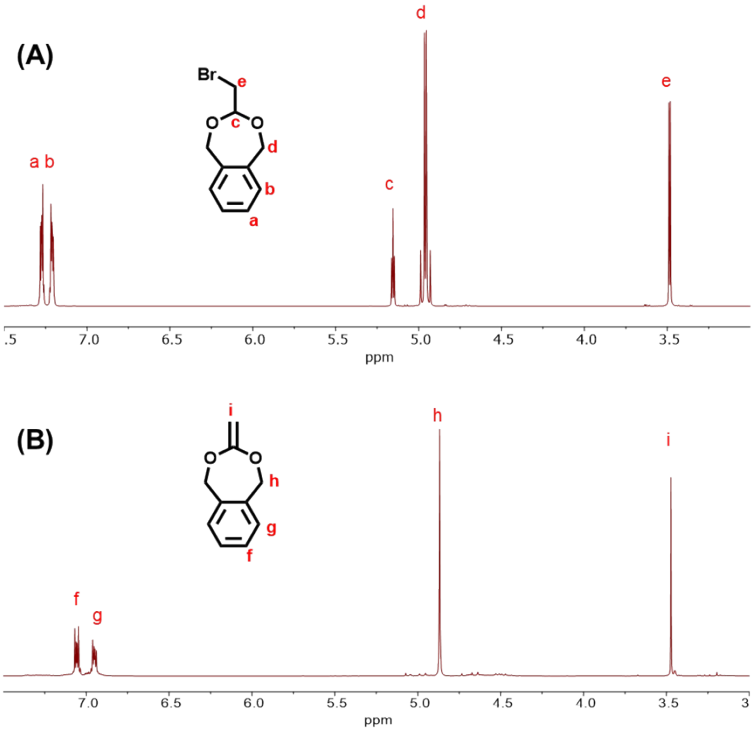
[‡]Authors contributed equally to this work.

*Correspondence to: yi-feng.du@basf.com, coughlin@mail.pse.umass.edu

Synthesis of *5,6*-benzo-*2*-methylene-*1,3*-dioxepane (BMDO)

Step 1: synthesis of 5,6-benzo-2-(bromomethyl)-1,3-dioxepane. 1,2-benzenedimethanol (147.1 g, 1.06 mol), bromoacetaldehyde dimethylacetal (180.0 g, 1.06 mol) were mixed as the stock solution. Dioxane (100 g) and *p*-toluenesulfonic acid (1.01 g, 10 mmol) was added to a pre-dried three-neck flask fitted with a Claisen bridge and dropping funnel for collecting methanol. Increase the temperature to 100 °C and start adding the stock solution dropwise over 5 h under nitrogen. Keep effectively recycling dioxane while removing the methanol. When almost all the calculated amount of methanol was collected, the temperature was raised to 120 °C under reduced pressure. After cooling at room temperature, the crude product solidified. The product was dissolved in $CHCl_2$ and washed with $NaHCO_3$ solution and water. The solution was then dried over $MgSO_4$, concentrated, and recrystallized in a mixture of chloroform and *n*-hexane to give 180.0 g (yield = 80 %) of pale-yellow crystals.

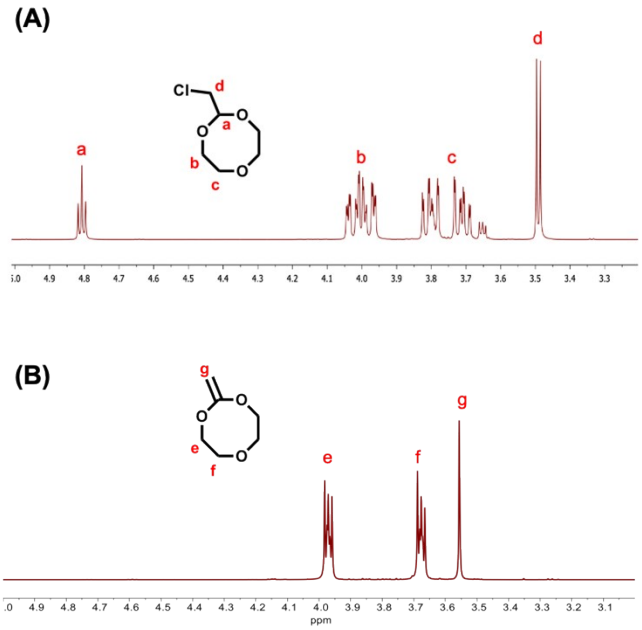
Step 2: synthesis of BMDO. A mixture of *5,6*-benzo-*2*-(bromomethyl)-*1,3*-dioxepane (180.0 g, 0.74 mol), *t*-BuOK (92.5 g, 0.96 mol) and 800 mL *t*-BuOH were added into a round-bottom flask and allowed to react under nitrogen at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into 2 L of diethyl ether. The insoluble material was removed by passing through Al_2O_3. The diethyl ether was removed, and the crude liquid was distilled under reduced pressure to give a colorless liquid which solidified to white crystals (92.0 g, yield = 77%).



Peak	δ (ppm)	Integration
a	7.4 - 7.3	2.0
b	7.3 - 7.1	2.0
c	5.2 - 5.1	1.0
d	5.0 - 4.9	4.1
e	3.5 - 3.4	2.0

Peak	δ (ppm)	Integration
f	7.1 - 7.0	2.0
g	7.1 – 6.9	2.0
h	4.9 – 4.8	3.6
i	3.5 – 3.4	1.8

Figure S1 ^{1}H NMR of (A) *5,6*-benzo-*2*-(bromomethyl)-*1,3*-dioxepane and (B) BMDO.



Peak	δ (ppm)	Integration
a	4.79	1.0
b	4.06 – 3.92	4.1
c	3.83 – 3.59	4.1
d	3.47	2.0

Peak	δ (ppm)	Integration
e	4.01 – 3.92	4.1
f	3.71 – 3.62	4.1
g	3.58 – 3.52	2.0

Figure S2. ^{1}H NMR of (A) *2*-(chloromethyl)-*1,3,6*-trioxocane and (B) MTC.

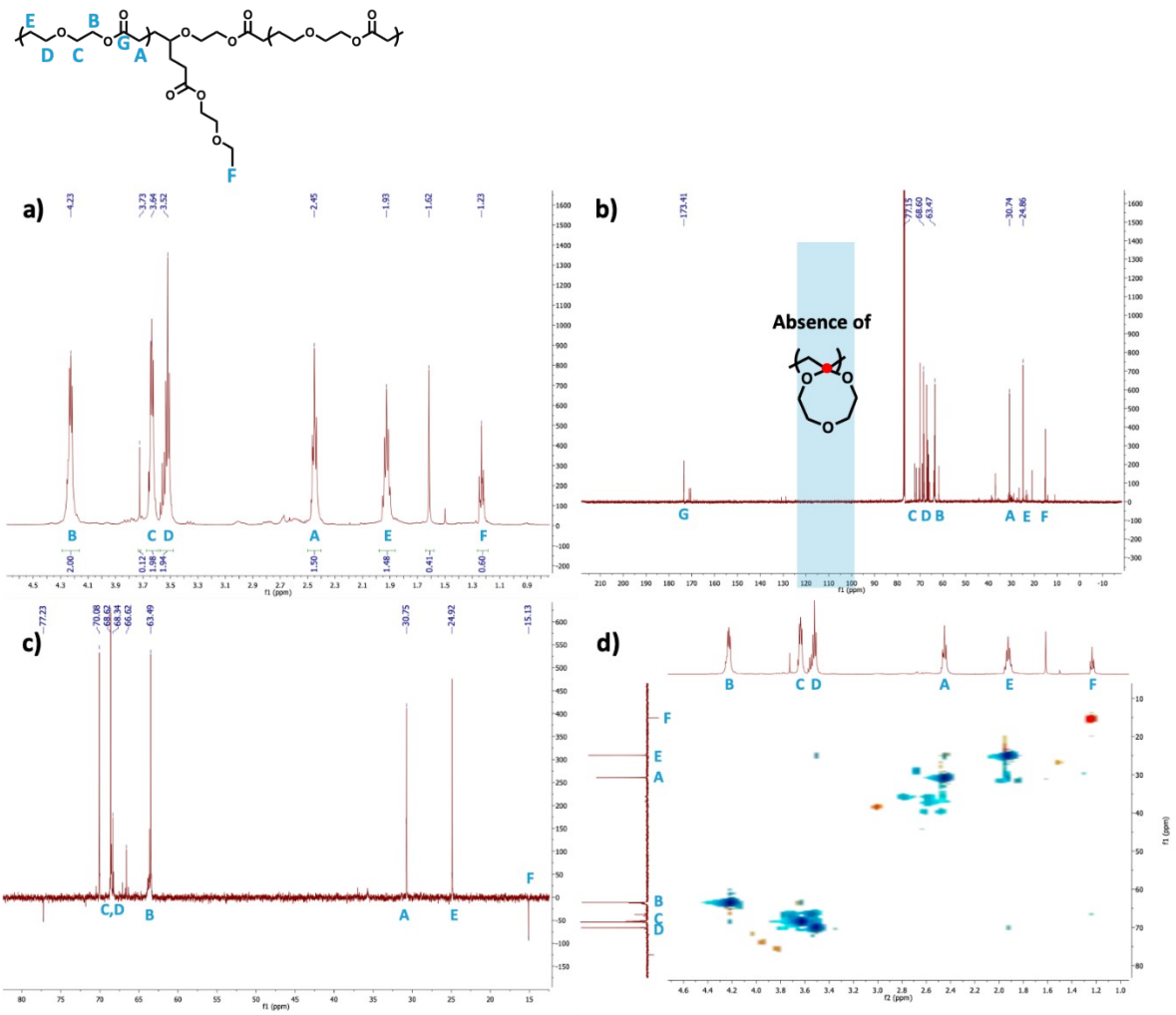


Figure S3 NMR characterization of poly(MTC). (a) ^{1}H NMR (b) ^{13}C NMR: no acetal carbon (100 ppm - 110 ppm) was observed, indicating 100% ring-opening of MTC (c) DEPT-135 (d) HMQC

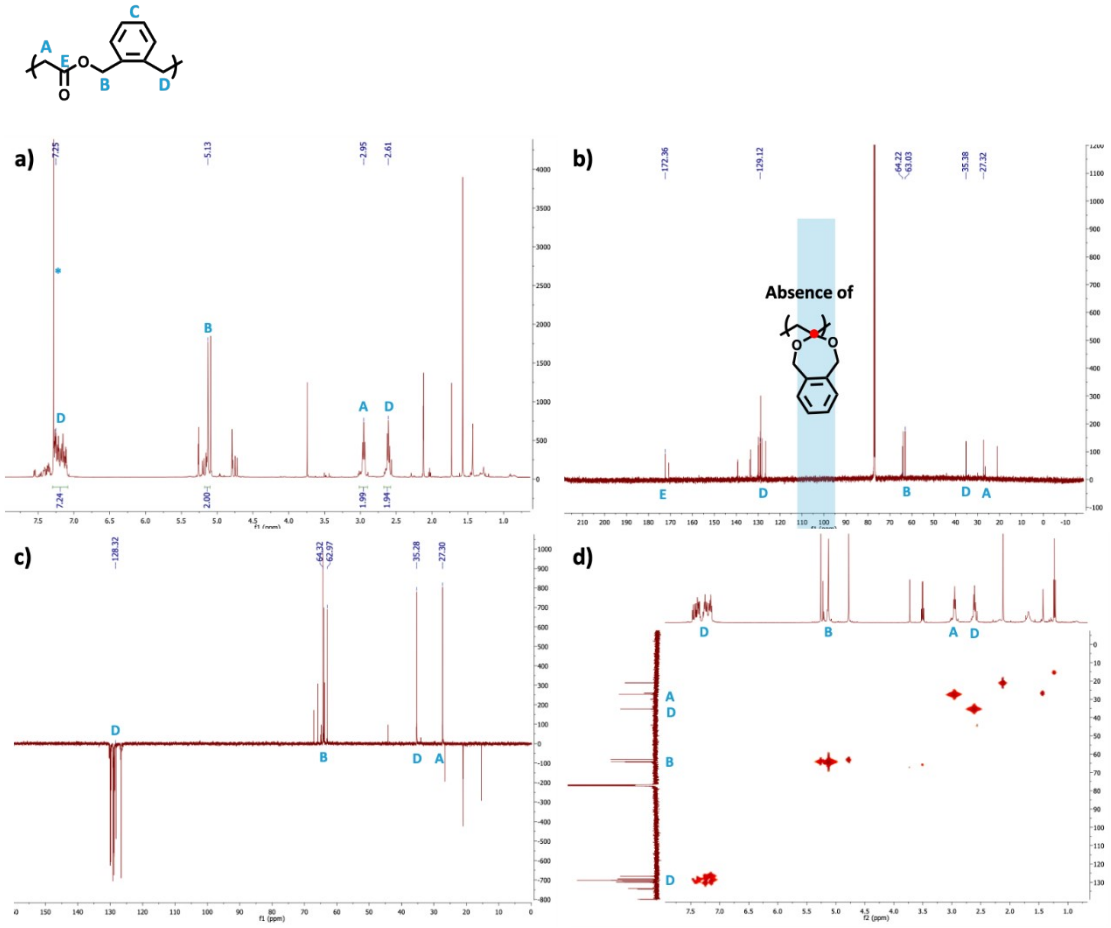


Figure S4 NMR characterization of poly(BMDO). (a) ^{1}H NMR (b) ^{13}C NMR: no acetal carbon (100 ppm - 110 ppm) was observed, indicating 100% ring-opening of MTC (c) DEPT-135 (d) HMQC

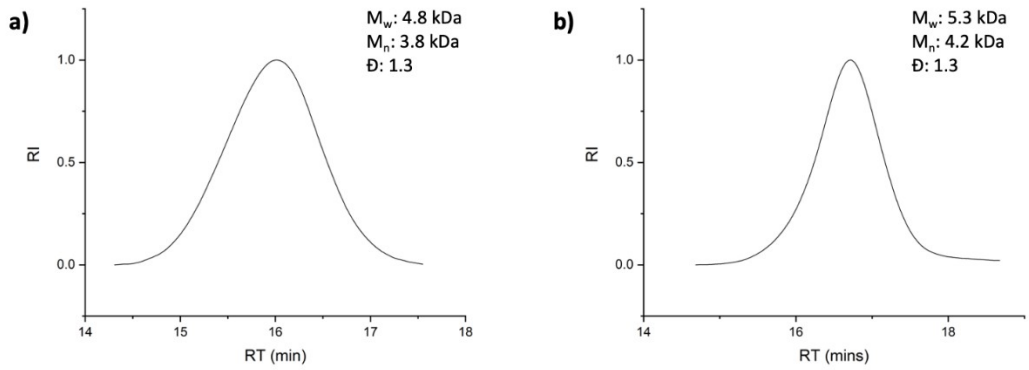


Figure S5 GPC characterization of a) poly(MTC) and b) poly(BMDO).

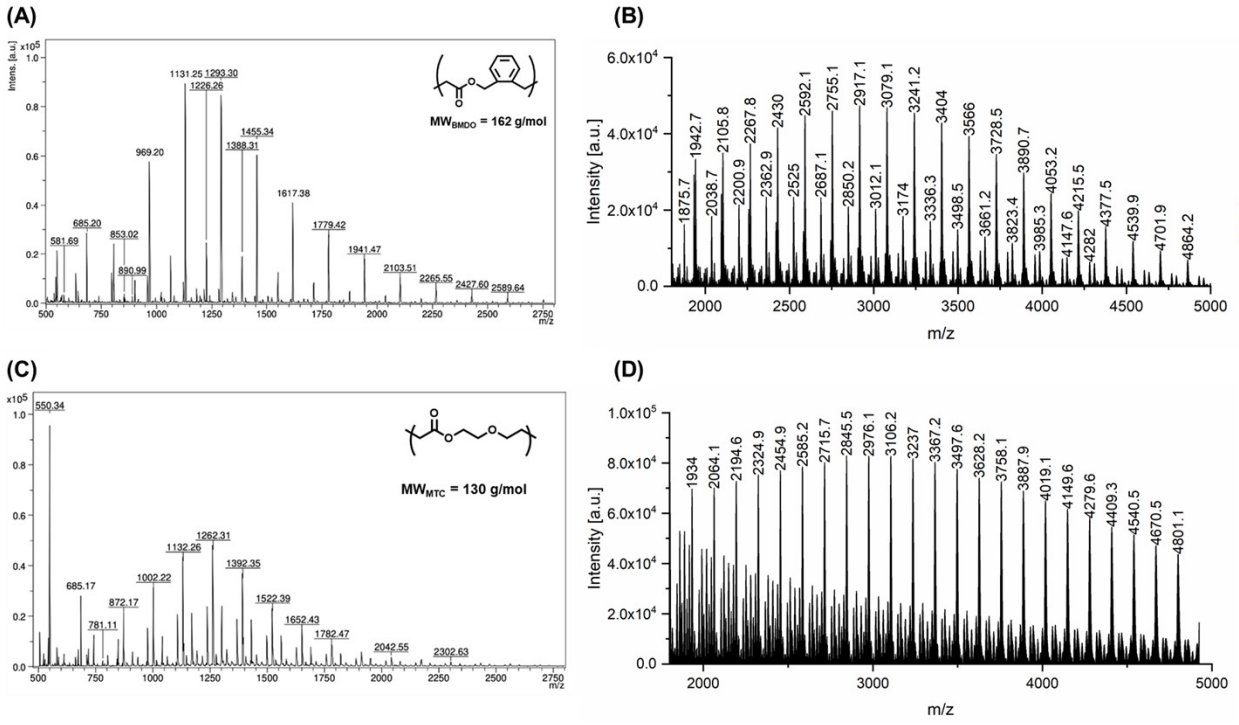
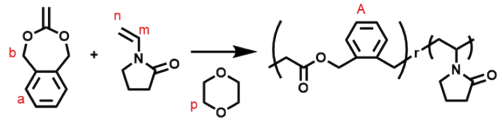


Figure S6 Full spectra of MALDI-TOF characterization of CKA homopolymers using various solvents, poly(BMDO) w/ (A) anisole or (B) dioxane, and poly(MTC) w/ (C) anisole or (D) dioxane.



Peak	δ (ppm)	Integration
A, a, m	7.46 .. 6.77	4.7
b	5.08 .. 4.91	4.0
n	4.40 .. 4.25	1.0
c, p	3.74 .. 3.48	29.5

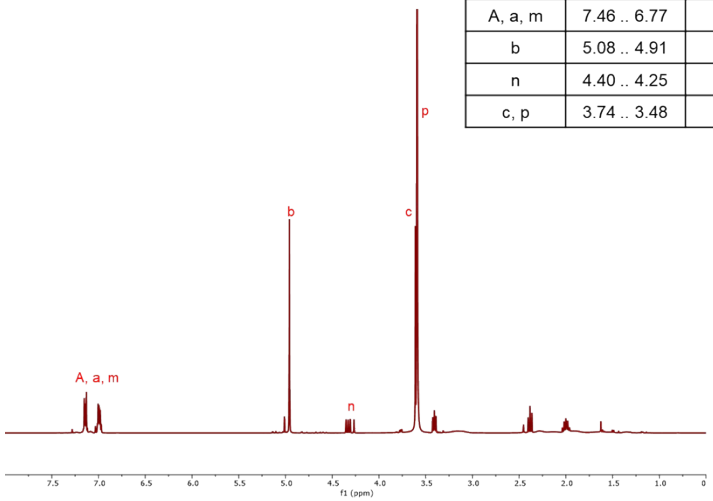
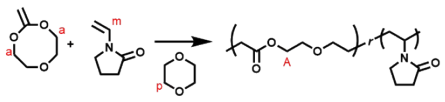


Figure S7 ^{1}H NMR assignments for a crude polymerization solution aliquot. The concentrations and conversions of BMDO and *N*VP can be calculated based on peak integrations.



Peak	δ (ppm)	Integration
m	7.10 .. 6.93	1.0
A	4.20 .. 4.06	6.0
a	4.05 .. 3.94	41.8
p	3.66 .. 3.50	666.0

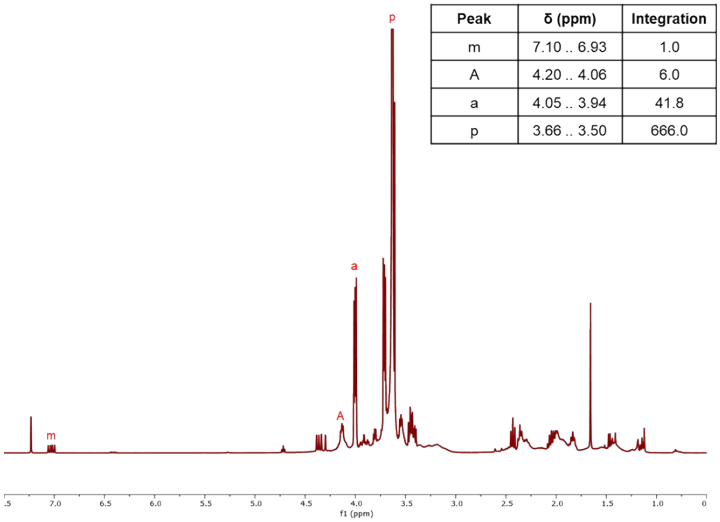


Figure S8 ^{1}H NMR assignments for a crude polymerization solution aliquot. The concentrations and conversions of MTC and *N*VP can be calculated based on peak integrations.

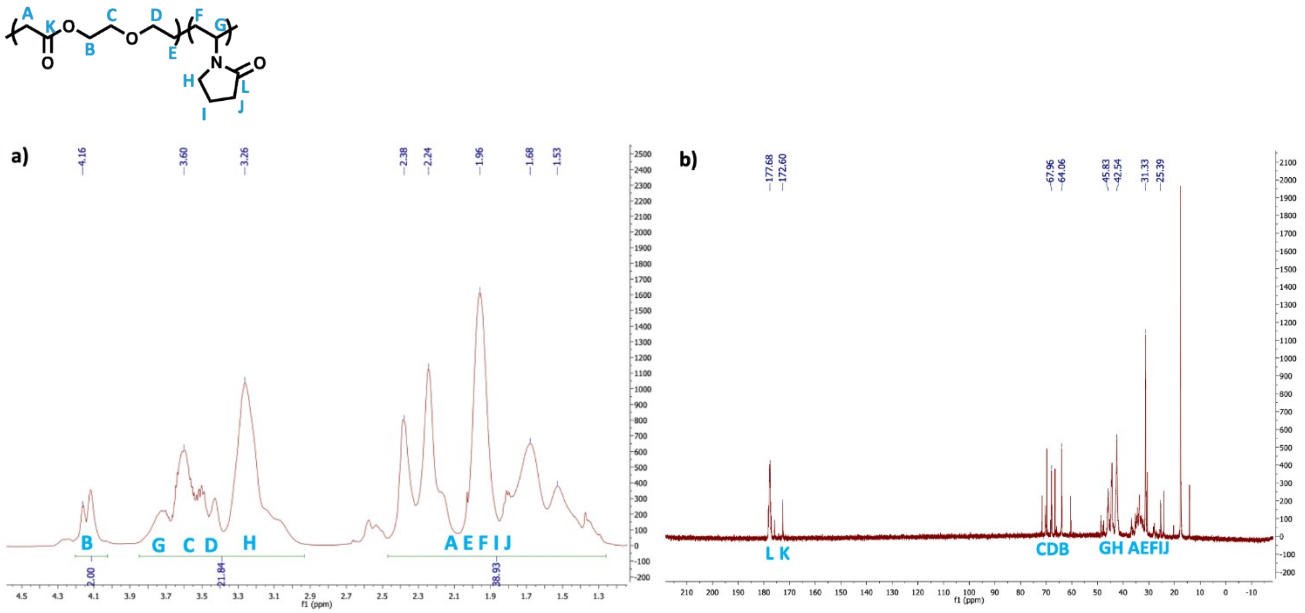


Figure S9 (a) ^{1}H NMR and (b) ^{13}C NMR of a poly(MTC-NVP).

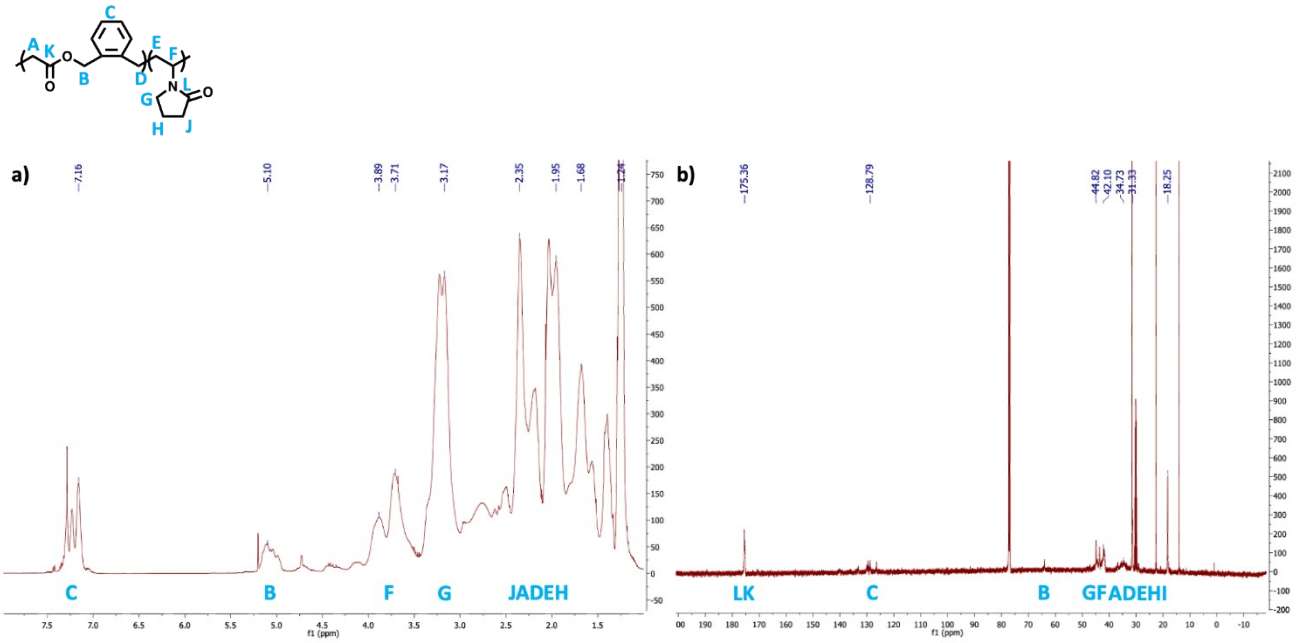


Figure S10 (a) ^{1}H NMR and (b) ^{13}C NMR of a poly(BMDO-NVP).

Table S1 Synthetic Parameters of the Semi-Batch Polymerization of CKA and *N*VP in dioxane.

Trial	T (ºC)	Initiator	BMDO : *N*VP	Initiator dosing	NVP dosing	BMDO dosing
(1)	80	AIBN	1 : 3	50% over 5h	100% 5h	-
(2)	100	^{t}BuPE	1 : 3	100% over 5h	100% 5h	-
(3)	100	^{t}BuPE	1 : 4	100% over 5h	100% 5h	-
Trial	T (ºC)	Initiator	MTC : *N*VP	Initiator dosing	NVP dosing	MTC dosing
(4)	80	AIBN	1 : 3	50% over 5h	100% 5h	-
(5)	80	AIBN	1 : 3	50% over 5h	100% 5h	50% over 3h
(6)	100	^{t}BuPE	1 : 3	100% over 5h	100% 5h	30% over 5h
(7)	100	^{t}BuPE	1 : 9	100% over 5h	100% 5h	80% over 5h

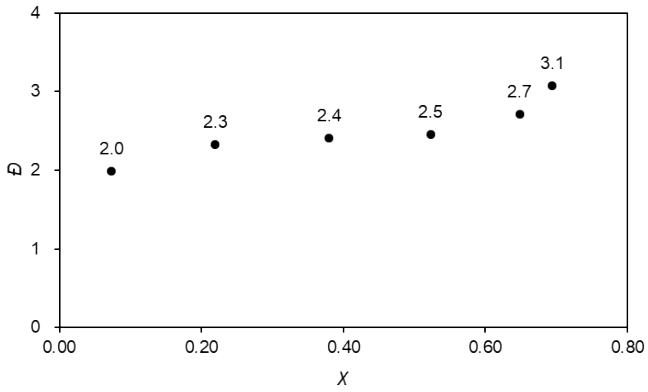


Figure S11 Polymer dispersity evolution with conversion (χ) for BMDO *N*VP semi-batch polymerization. (Trial 1, initiator: AIBN, 80 ºC, initiator and *N*VP dosing over 5 h)

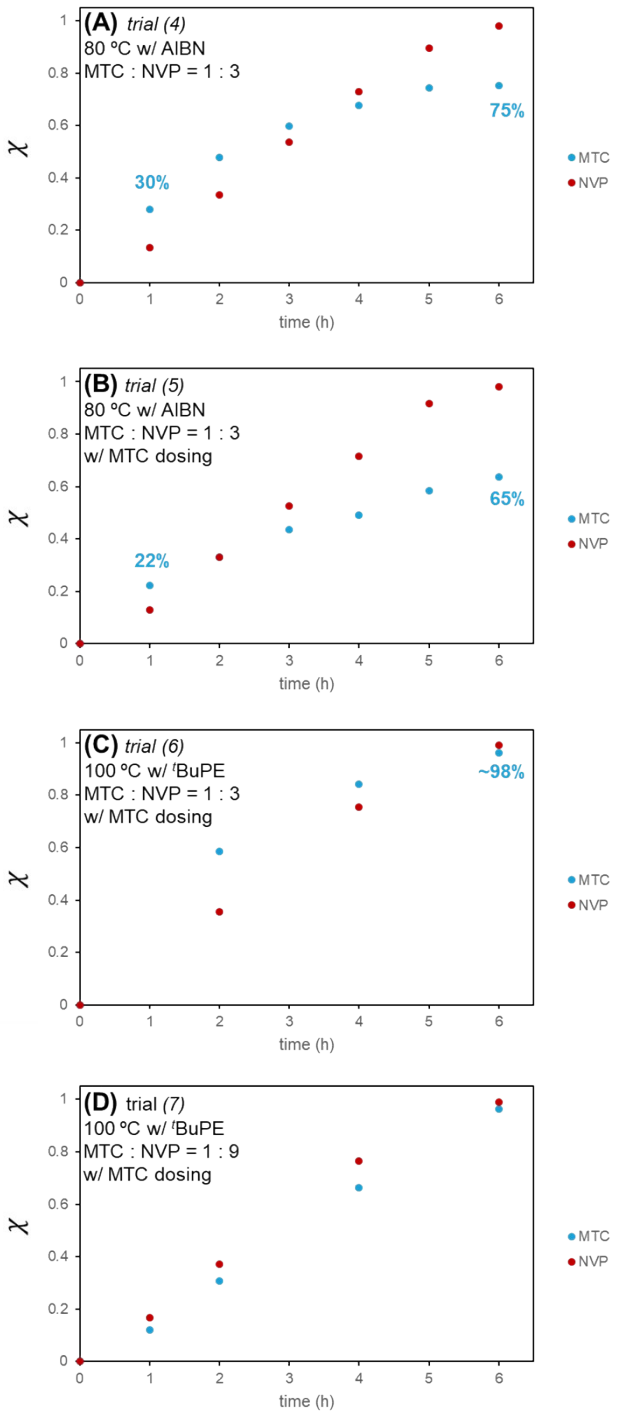


Figure S12 Monomer conversion (χ) vs. time (A-D) and scientific monomer conversion vs. time (E-H) of MTC *N*VP semi-batch polymerizations, following trials (4-7).

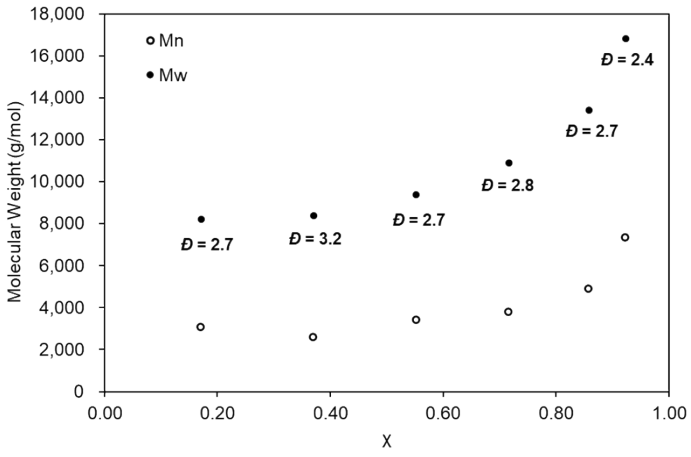


Figure S13 Polymer molecular weight change with conversion (χ) characterized with GPC for MTC, NVP semi-batch polymerization.

(Trial 4, initiator: AIBN, 80 °C, initiator and *N*VP dosing over 5h)

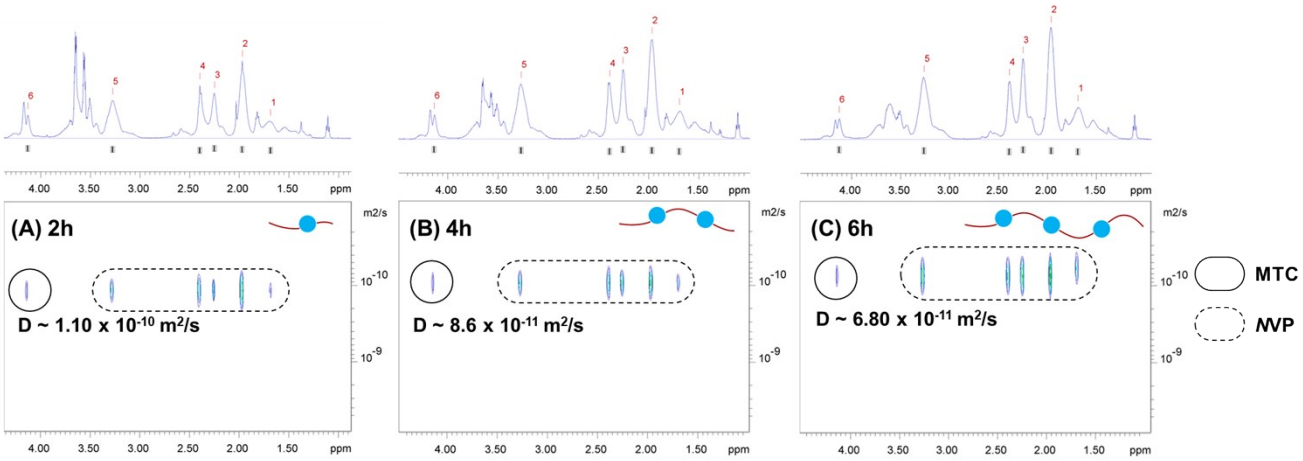


Figure S14 The change of polymer compositions and diffusion coefficients over time, monitored using DOSY for MTC, NVP semi-batch polymerization.

(Trial 4, initiator: AIBN, 80 °C, initiator and *N*VP dosing over 5h)

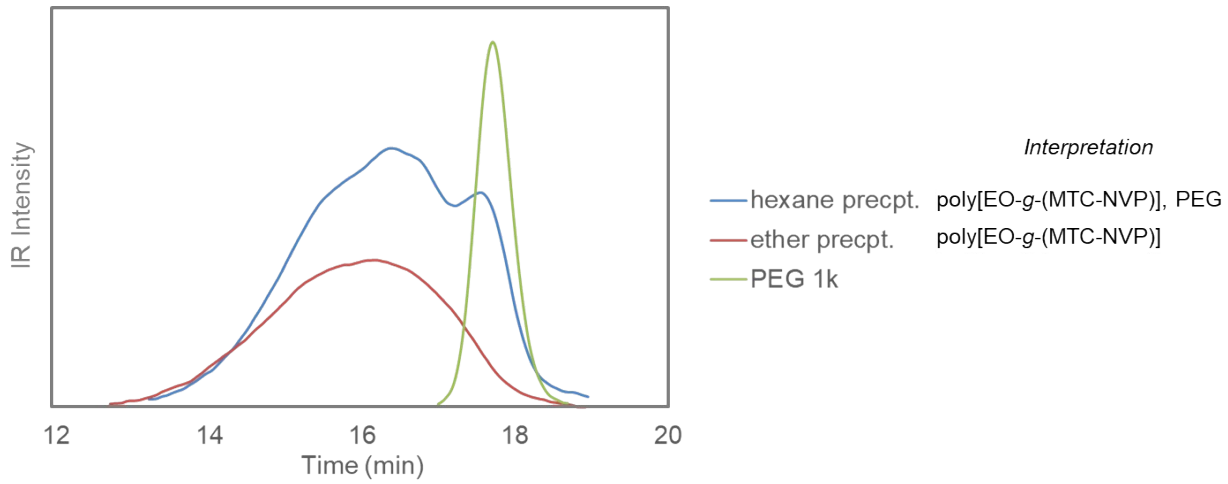


Figure S15 GPC characterization demonstrates the effective removal of un-grafted PEG via diethyl ether fractionation.

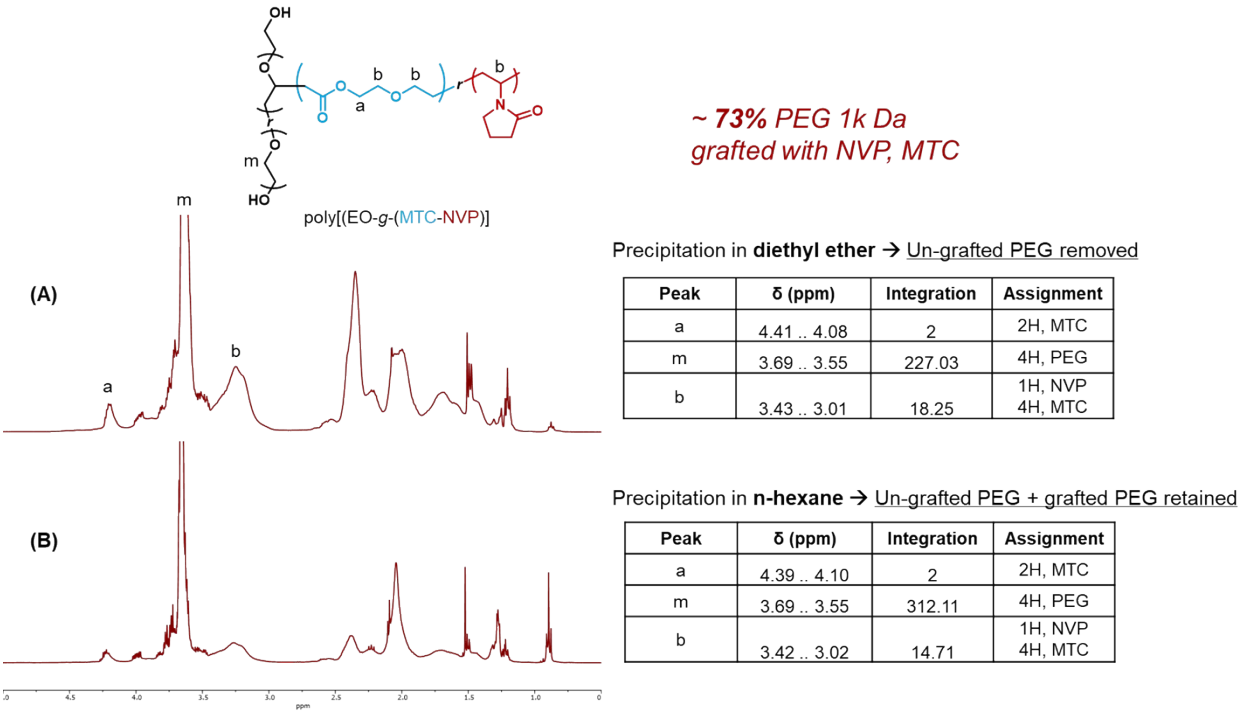


Figure S16 ^{1}H NMR characterization of a PEG grafted CKA NVP copolymer. The grafting ratio can be calculated based on the integration change of PEG moieties in (A) diethyl ether precipitate and (B) n-hexane precipitate, respectively.

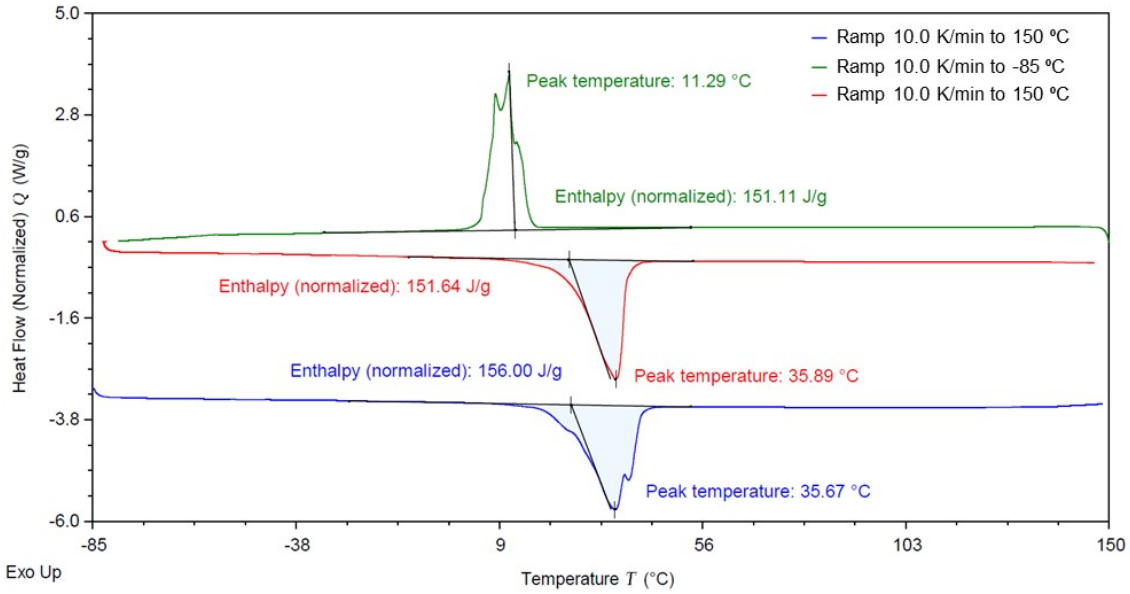


Figure S17 DSC characterization of PEO.

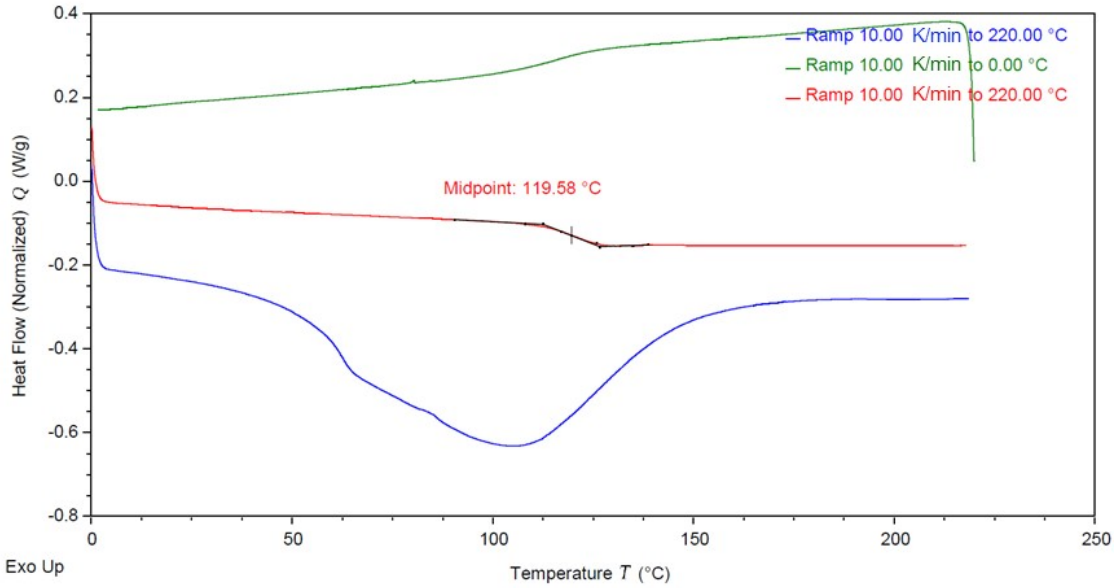


Figure S18 DSC characterization of poly(BMDO$_n$-NVP$_{3n}$).

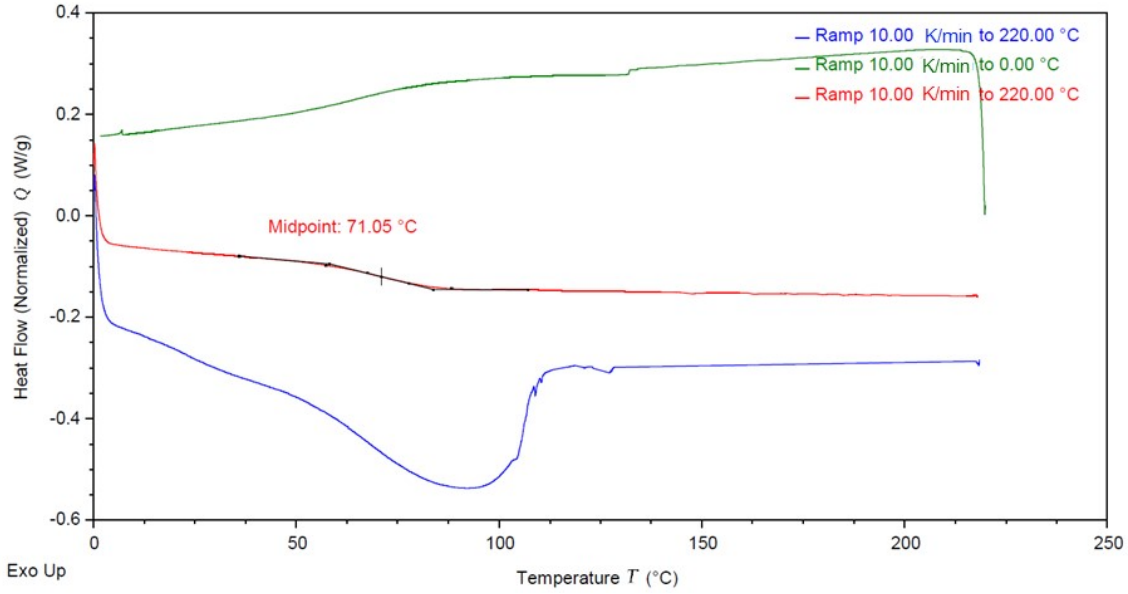


Figure S19 DSC characterization of poly(MTC$_n$-NVP$_{3n}$).

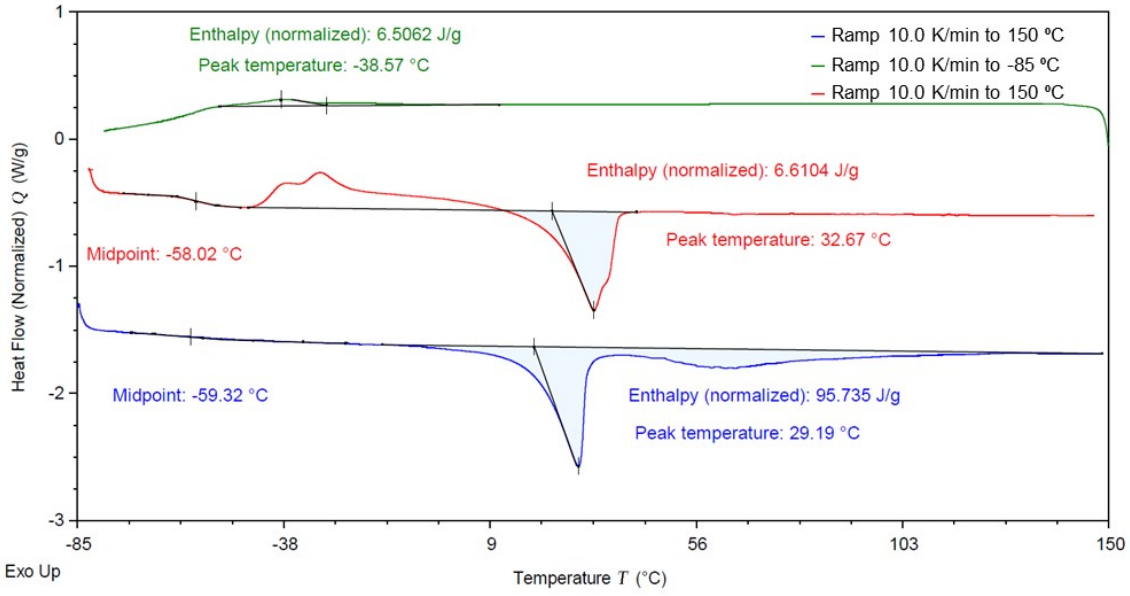


Figure S20 DSC characterization of poly[(EO$_{1k}$-*g*-(MTC$_n$-NVP$_{3n}$)]_PEO 70 wt%.

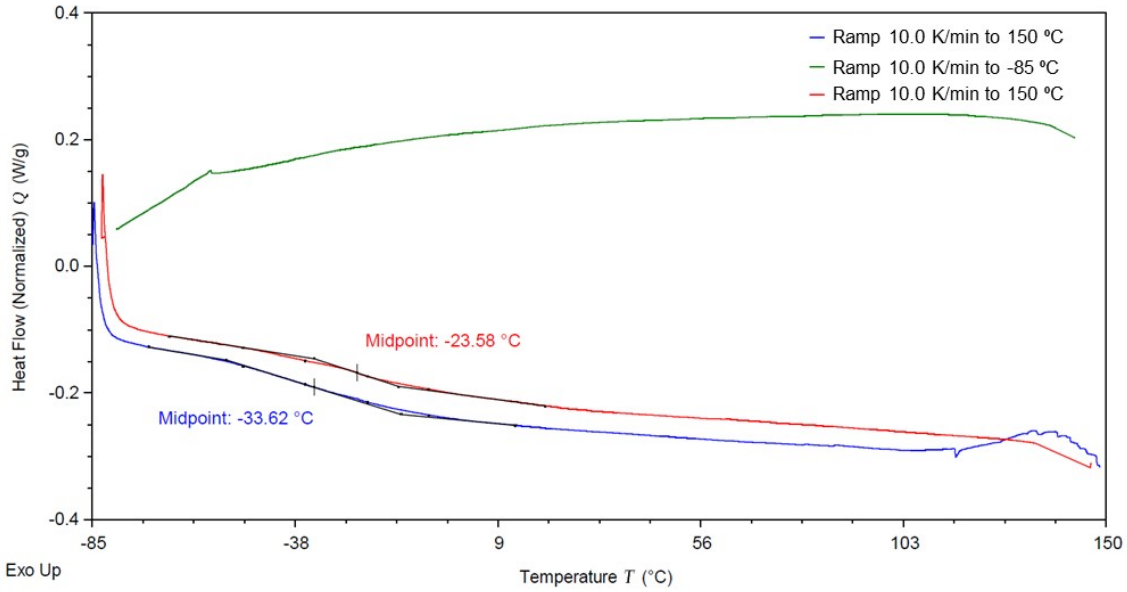


Figure S21 DSC characterization of poly[(EO_{1k}-*g*-(MTC_n-NVP_{3n})]_PEO 30 wt%.