Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Facile Synthesis of Norbornene-Ethylene-Vinyl Acetate/Vinyl Alcohol Multiblock Copolymers by the Olefin Cross-Metathesis of Polynorbornene with Poly(5-acetoxy-1-octenylene)

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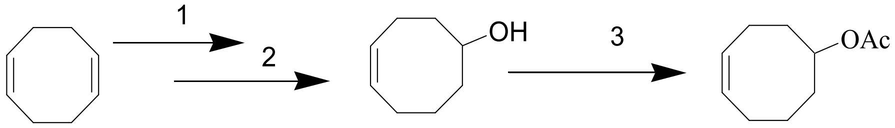
Monomer synthesis. 5-Substituted cyclooctenes were prepared according to the published procedures.[31,40] 5-Hydroxy-1-cyclooctene (COH) was synthesized by epoxidation of 1,5-cyclooctadiene (COD) in the presence of m-chloroperbenzoic acid (mCPBA) and subsequent reduction of the resulting 5,6-epoxy-1-cyclooctene (ep-CO) with $LiAlH_4$. The ^1H NMR and GC–MS spectra of COH were in agreement with the literature data.

To prepare 5-acetoxy-1-cyclooctene (COAc), COH (5.21 g, 0.041 mol) was placed into a 100 mL three-necked flask equipped with a reflux condenser, a magnetic stirrer, and a dropping funnel, then 52 mL of dry pyridine was added with stirring. The resulting solution was cooled with an ice bath and 6.5 mL (0.09 mol) of acetyl chloride was added dropwise for 30 min with constant stirring. After removing the ice bath, the reaction mixture was stirred for 2 h at room temperature. The system was diluted with Et_2O (50 mL) and a 10 ml 1M HCl was added dropwise. Then, it was washed with a saturated $NaHCO_3$ solution (10 mL) and three times with water (30 mL). The organic layer was decanted, dried over $MgSO_4$, and concentrated under reduced pressure. The resulting colorless oil was purified by distillation over CaH_2 (b.p. = 42–44 °C at 0.4 Torr) and stored under argon. COAc yield was 2.76 g (53 %), purity 99.9% by GC.

^1H NMR (600 MHz, $CDCl_3$) δ, ppm: 5.7–5.57 (m, 2H, CH=CH); 4.83–4.77 (m, 1H, CH-OAc), 2.31 (1H, m, CH_2), 2.21–2.02 (m, 3H, CH_2), 1.99 (s, 3H, $C(O)CH_3$), 1.85 (2H, m, CH_2), 1.69 (1H, m, CH_2), 1.58 (3H, m, CH_2)



Scheme S1. Synthesis of 5-acetoxy-1-cyclooctene: (1) $CHCl_3$, m-chloroperbenzoic acid; (2) THF, $LiAlH_4$; (3) Py, AcCl

Polymerization. ***Poly(5-acetoxy-1-octenylene)*** (PCOAc) was synthesized by ROMP according to the following general procedure. G2 catalyst (6.7 mg, 0.0079 mmol) was placed in a round-bottom two-neck flask equipped with a magnetic stirrer and filled with argon. After adding 0.24 mL of dry $CHCl_3$ and 5.3 g (31.5 mmol) of COAc, the reaction was carried out for 24 h and stopped by adding ethyl vinyl ether (500 mol/mol to Ru) to the reaction mixture and stirring for 30 min. Then, an oxidation inhibitor (0.1 wt% per polymer) was added. The polymer was precipitated from chloroform solution with methanol and dried under reduced pressure at room temperature until constant mass. The yield of PCOAc was 4.6 g (86%). Structure of the obtained homopolymer corresponds to the literature data.[40]

^1H NMR (600 MHz, $CDCl_3$, Figure S1) δ, ppm: 5.36, 5.32 (2H, CH=CH); 4.86 (1H, CHO), 2.03–1.96 (7H, CH_3, CH_2); 1.52 (4H, CH_2); 1.34 (2H, CH_2)

^{13}C NMR (150.9 MHz, $CDCl_3$, Figure S2) δ, ppm: 170.89 (C=O); 130.52, 130.36, 129.95, 129.78 (trans CH=**C**H), 130.04, 129.86, 129.48, 129.28 (cis **C**H=**C**H); 73.94, 73.89, 73.85, 73.82 (HCO);

34.24, 34.17, 34.11, 33.97, 33.93, 33.89, 33.79, 32.53, 28.56, 27.16, 27.12, 25.48, 25.45, 25.42, 25.39, 25.35, 25.31, 23.36, 23.31 (CH_2); 21.37 (CH_3)

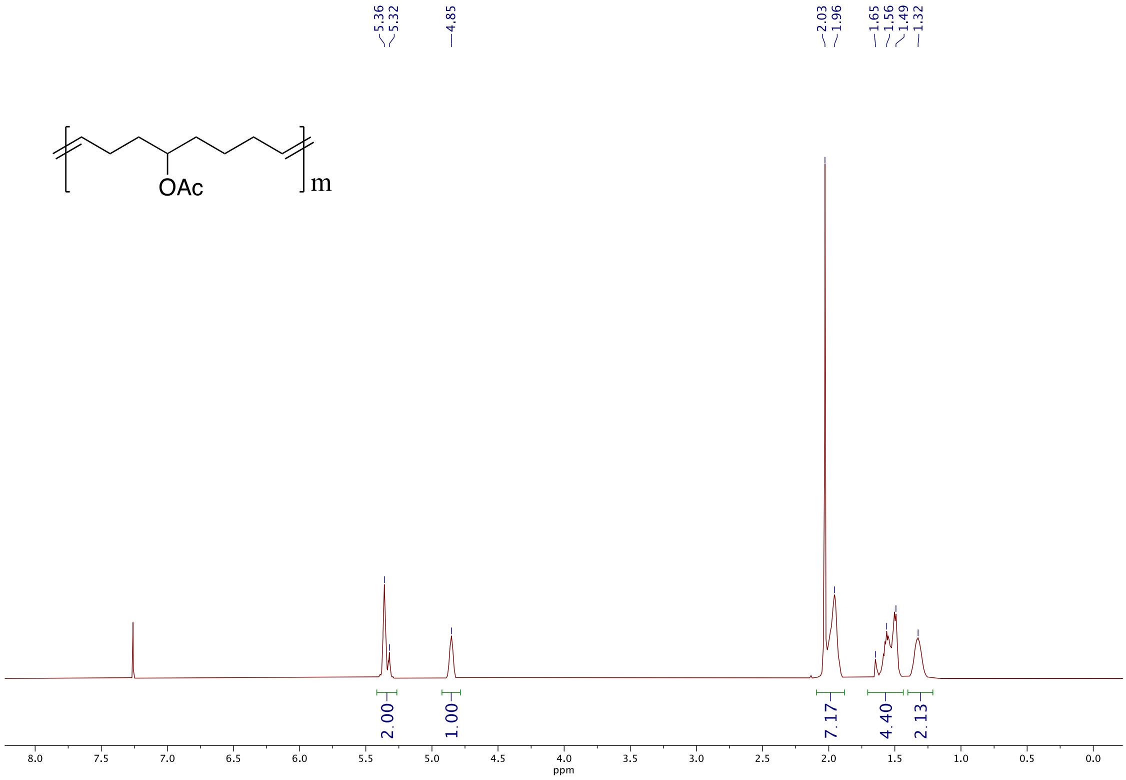


Figure S1. ^{1}H NMR spectrum of PCOAc at room temperature

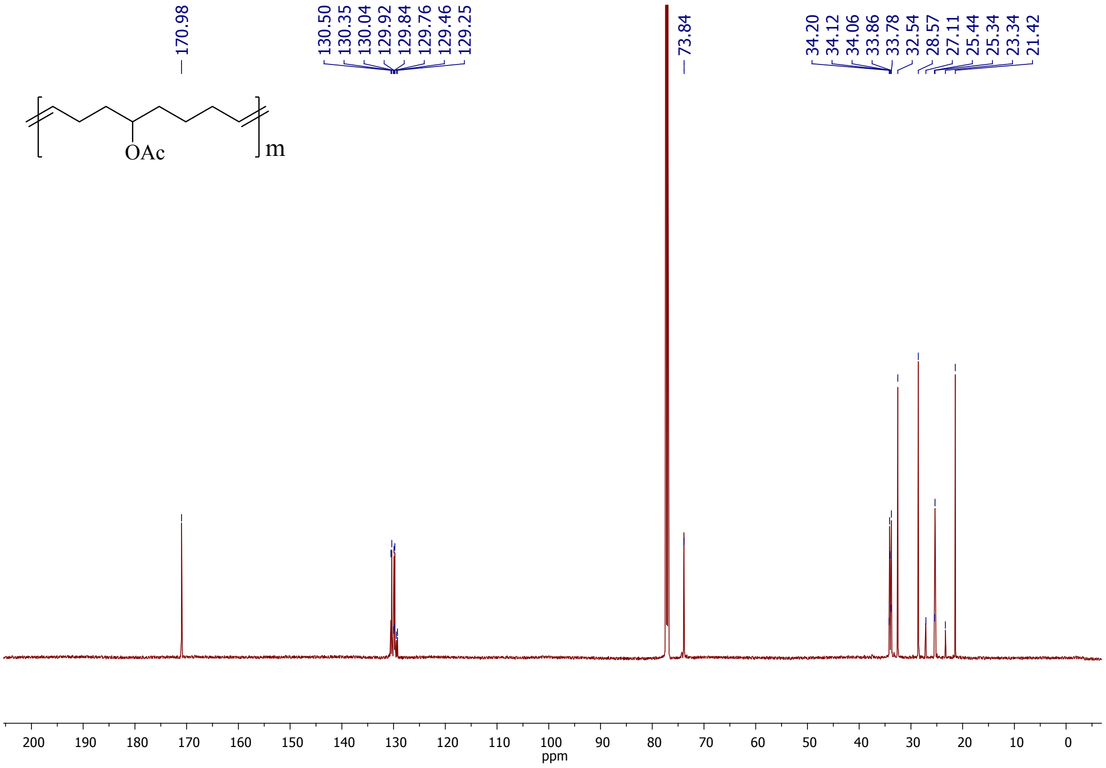


Figure S2. ^{13}C NMR spectrum of PCOAc at room temperature

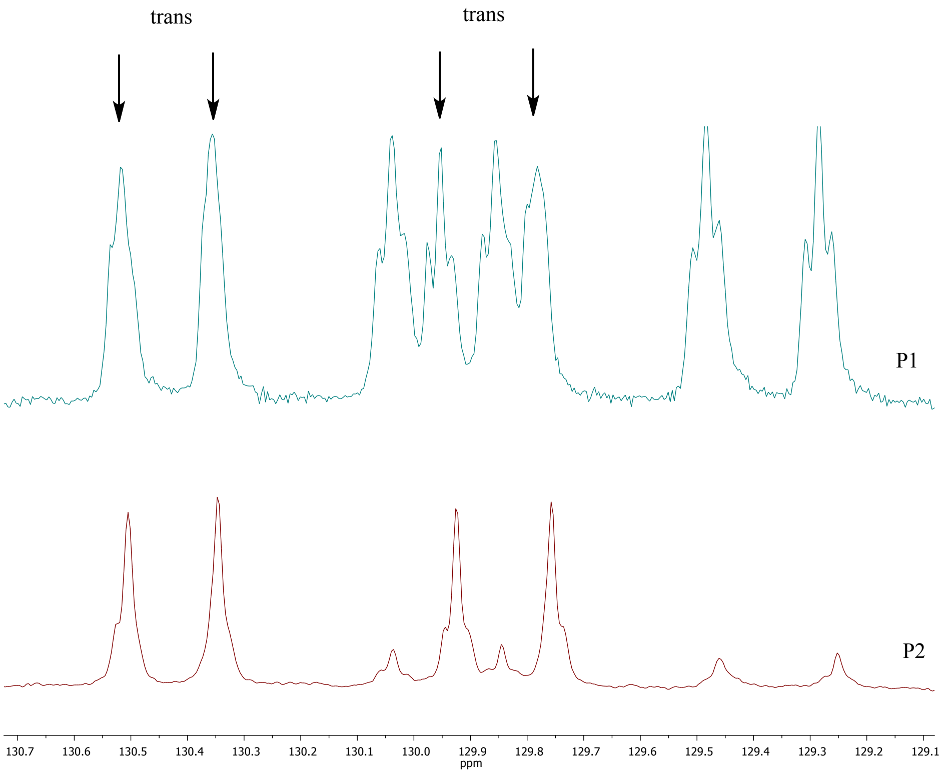


Figure S3. C=C double bond region of the ^{13}C NMR spectra (room temperature) of PCOAc synthesized in the presence of the (P1) G1 and (P2) G2 catalysts

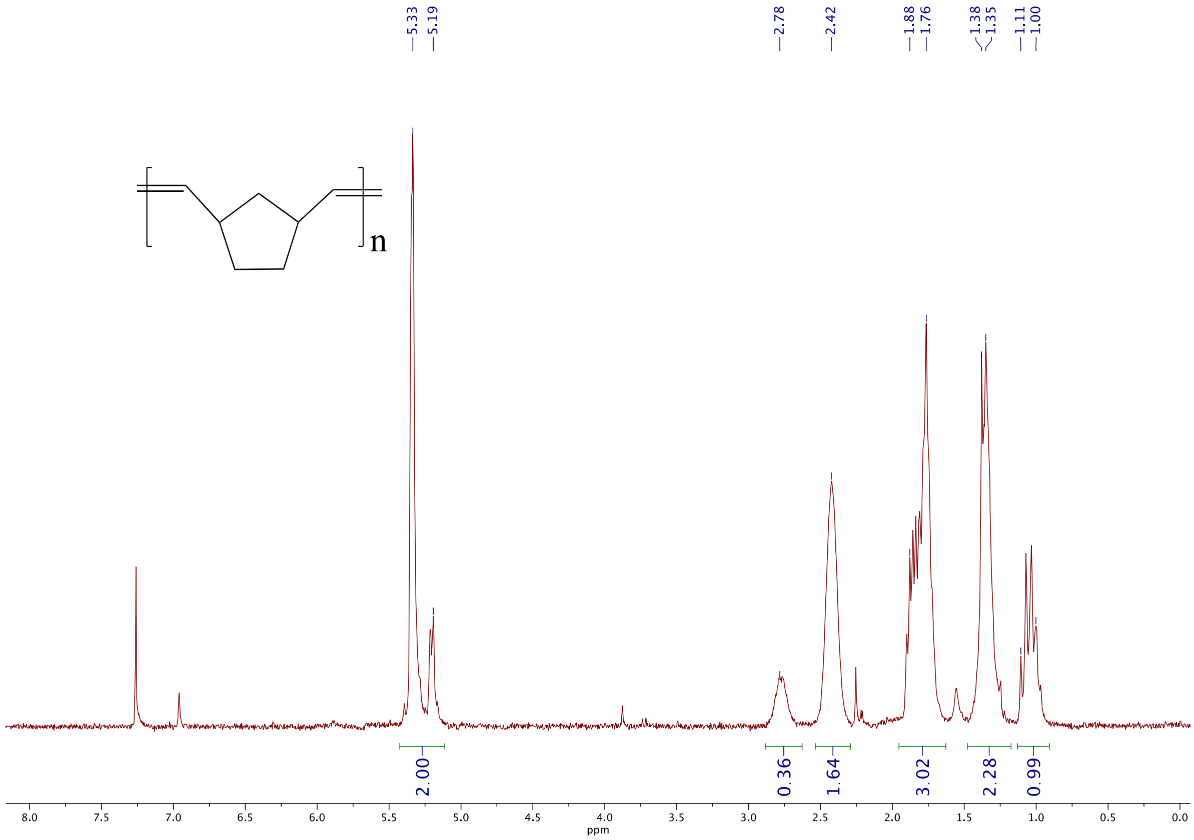


Figure S4. ^{1}H NMR spectrum of PNB at room temperature

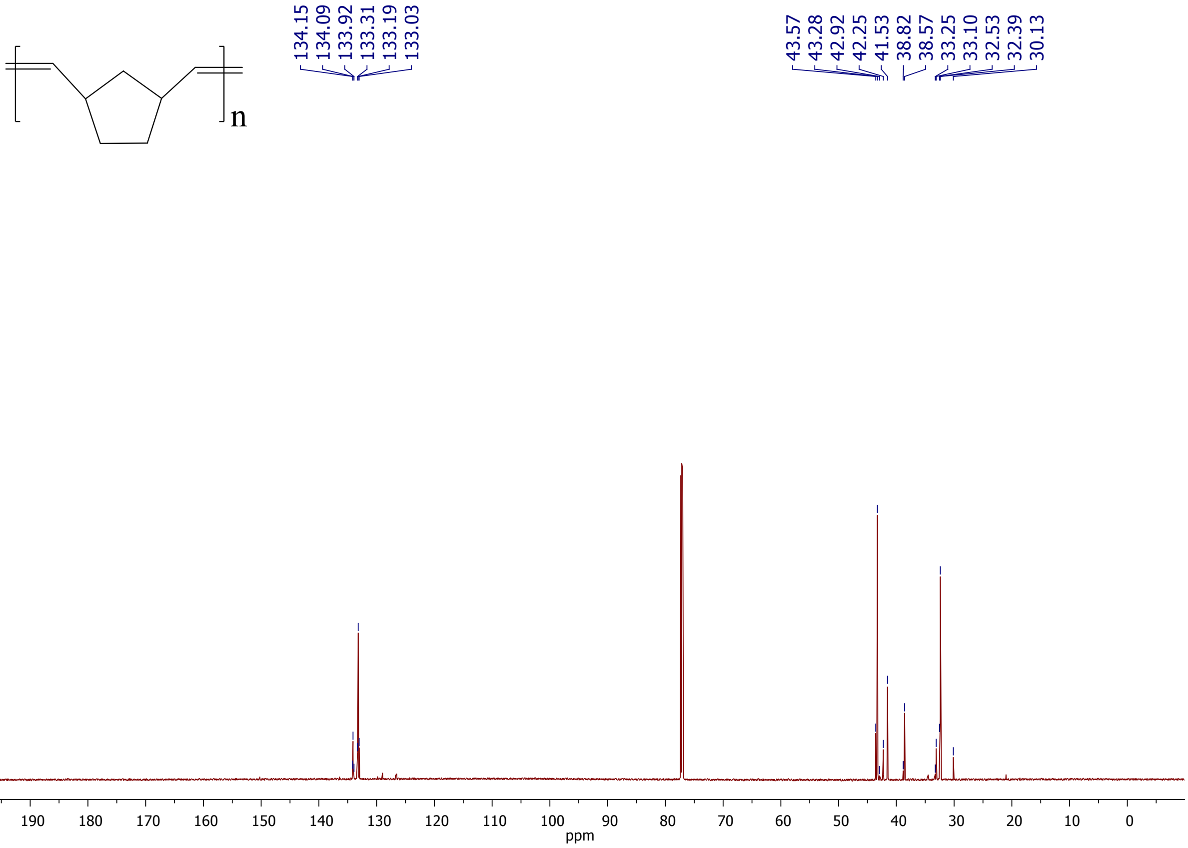


Figure S5. ^{13}C NMR spectrum of PNB at room temperature

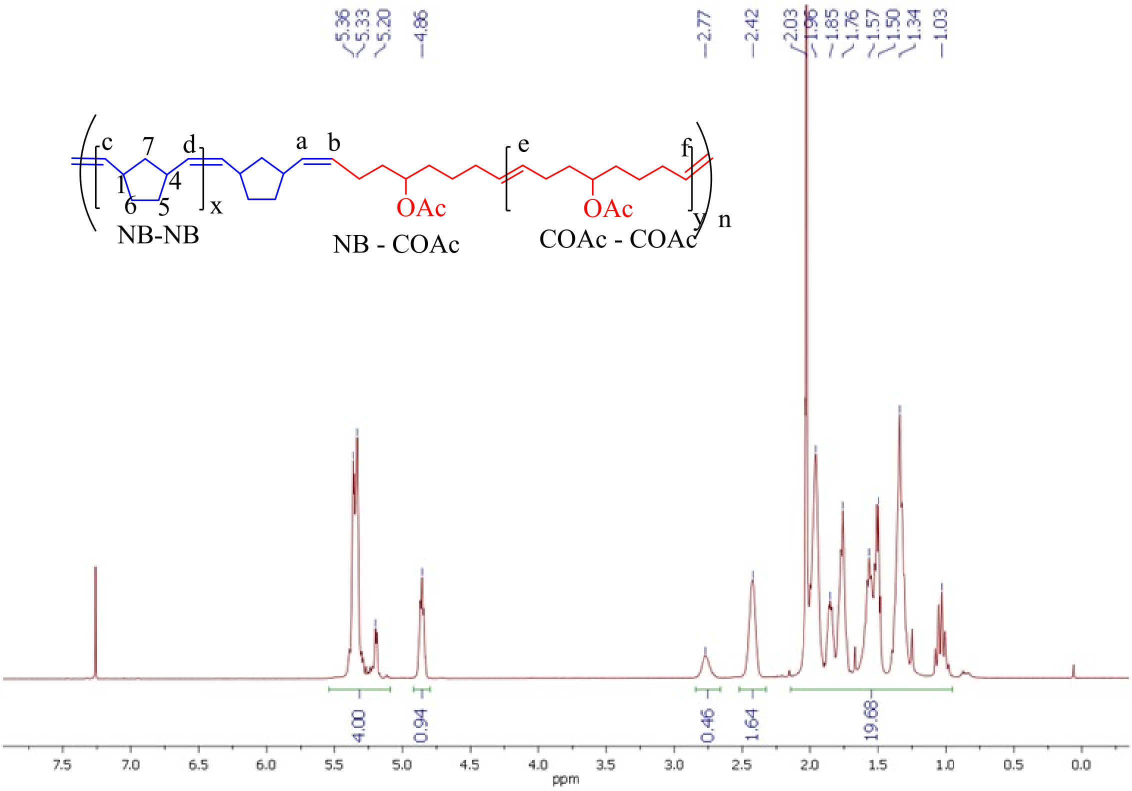


Figure S6. ^{1}H NMR spectrum of NB–COAc multiblock copolymer at room temperature

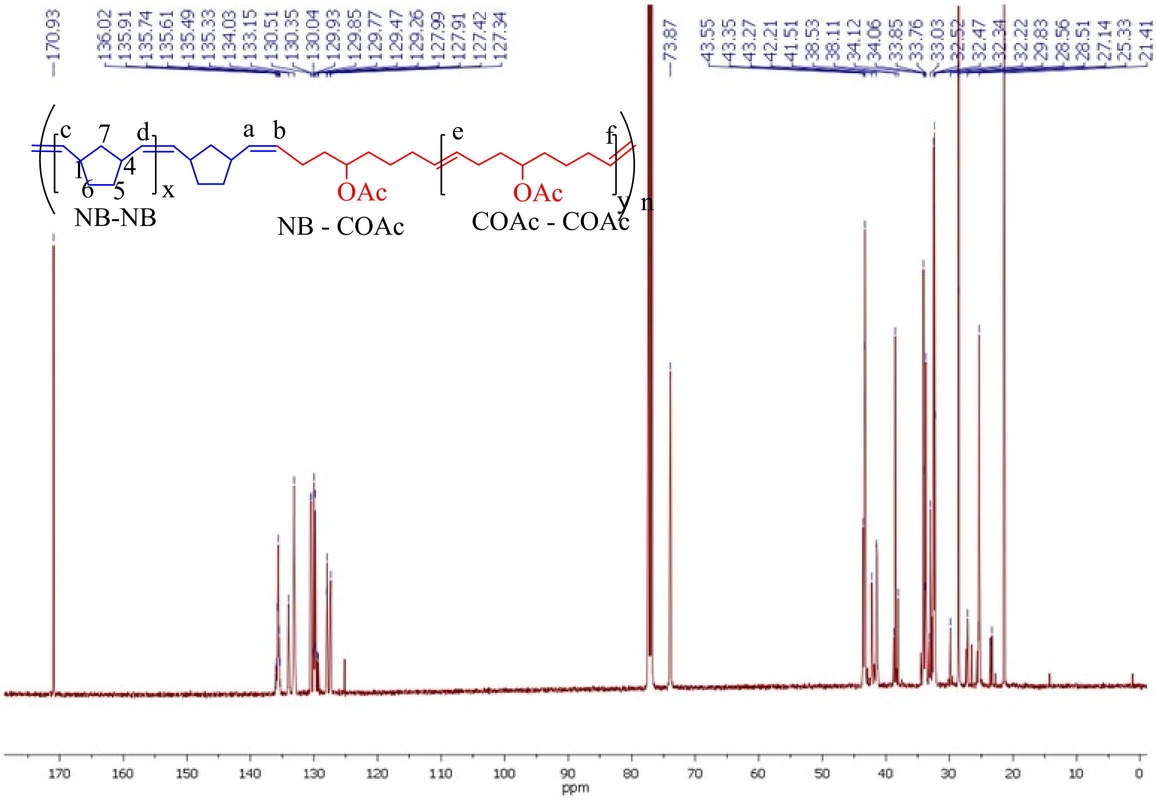


Figure S7. ^{13}C NMR spectrum of NB−COAc multiblock copolymer at room temperature

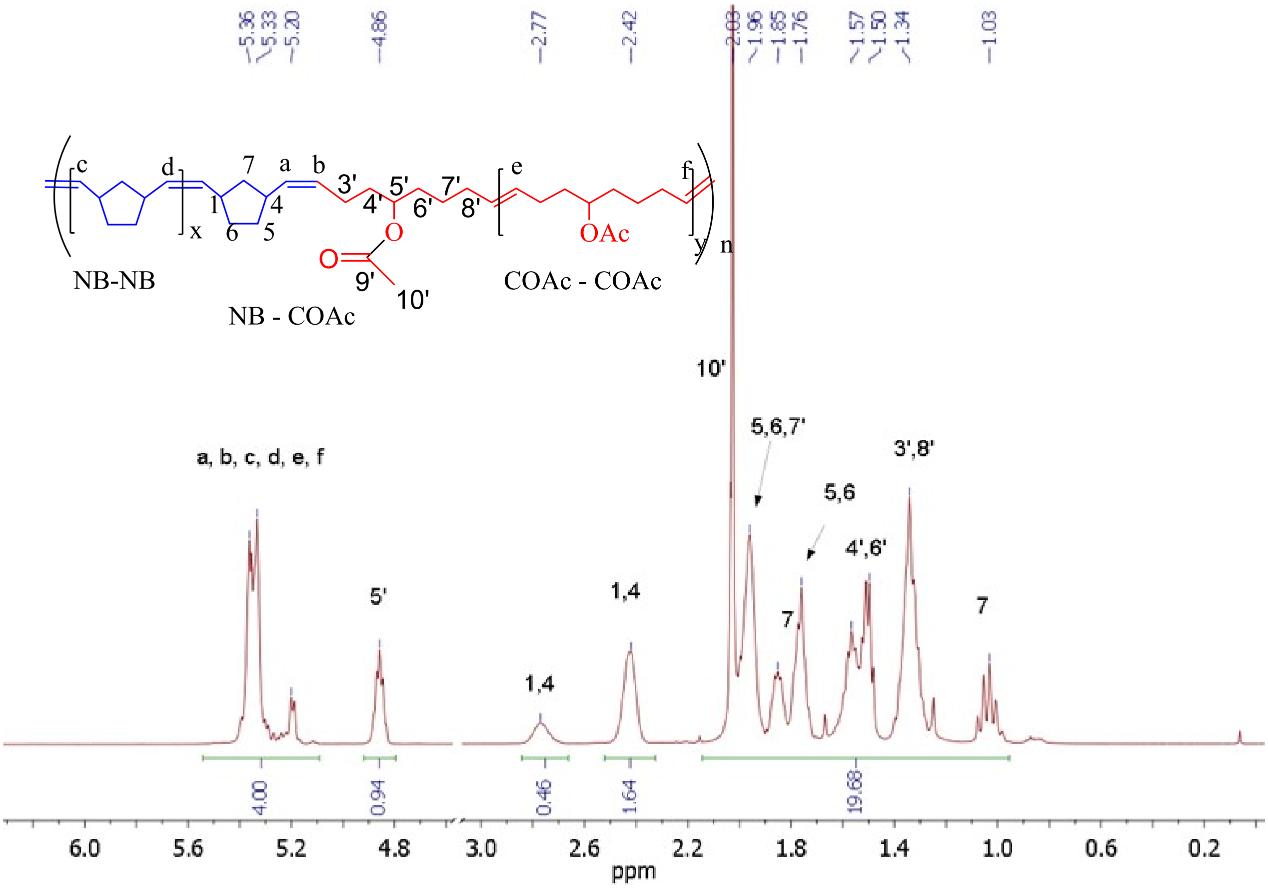


Figure S8. ^{1}H NMR spectrum (expanded regions) of NB−COAc multiblock copolymer at room temperature

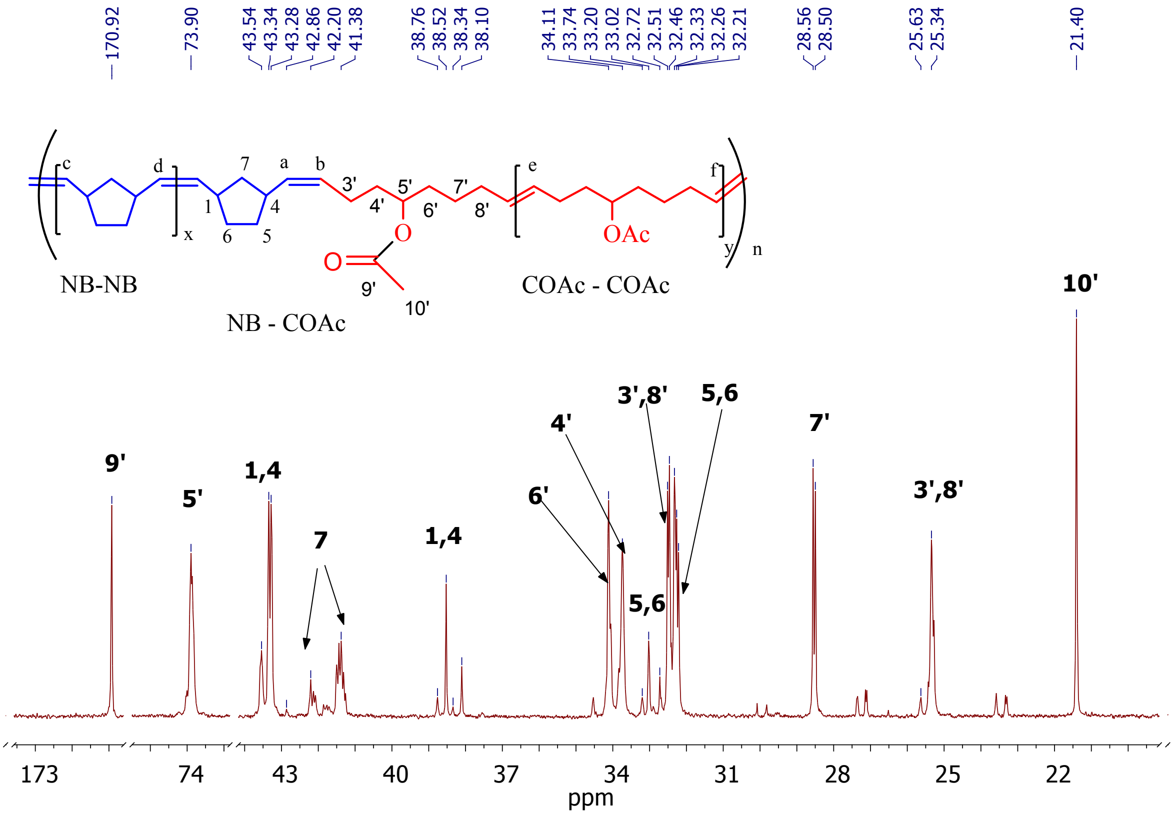


Figure S9. ^{13}C NMR spectrum (expanded regions) of NB–COAc multiblock copolymer at room temperature

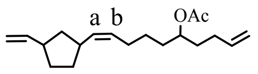
Table S1. Assignment of ^{13}C and ^{1}H NMR shifts of P(NB–COAc)

	C atom number	^{1}H, δ, ppm	^{13}C, δ, ppm	Comments
1	9’	-	170.92	(CH_3-**C**=O)
2	a	5.35	136.01, 135.90, 135.73, 135.60, 135.52, 135.49, 135.39, 135.34	C^a=, heterodyads NB–COAc
3	c, d	5.20	134.08, 134.02, 133.92	C^c=C^d, homodyads *cis*-NB–NB
4	c, d	5.33	133.21, 133.14, 133.07	C^c=C^d, homodyads *trans*-NB–NB
5	e, f	5.36	130.51, 130.36, 129.93, 129.77	C^e=C^f, homodyads *trans*-COAc–COAc
6	e, f		130.03, 129.85, 129.46, 129.26	C^e=C^f, homodyads *cis*-COAc–COAc
7	b	5.34	127.98, 127.90, 127.41, 127.34	C^b=, heterodyads COAc–NB
8	5’	4.86	73.90	s, 1H, CH-O-, PCOAc
9	1,4	2.42	43.54, 43.34, 43.28	s, 1H, C***H***-CH=CH *trans*-PNB
10	7	1.07, 1.05, 1.03, 1.01	42.86, 42.20, 42.13, 42.08	m, 1H, PNB
11	7	1.85	41,50, 41.44, 41.38, 41.31, 41.26	m, 1H, PNB
12	1,4	2.77	38.76, 38.52,	s, 1H, C***H***-CH=CH *cis*-PNB

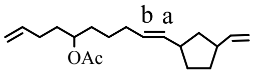
			38.34, 38.10	
13	6’	1.56	34.11	2H, PCOAc
14	4’	1.51	33.74	2H, PCOAc
15	5,6	1.76	33.20, 33.02	m, 2H, PNB
16	3’,8’	1.34	32.72, 32.51, 32.46	m, 2H, PCOAc
17	5,6	1.96	32.33, 32.26, 32.21	m, 2H, PNB
18	7’	1.96	28.56, 28.50	m, 2H PCOAc
19	3’,8’	1.34	25.63, 25.34	m, 2H PCOAc
20	10’	2.02	21.40	s, 3H, C(O)-C$\boldsymbol{H}_3$, PCOAc

Table S2. Characteristics of NB–COAc copolymers obtained from their ^{13}C NMR spectra

Copolymer (Run in Table 2)	Cat	L_{NB}	L_{COAc}	Trans-C=C in homo-dyads,%		Composition of NB–COAc dyads, %					Composition of COAc–NB dyads, %			
				NB	CO Ac	136.03 135.92	135.76	135.62	135.47	135.33	129.61	127.91 127.99	127.34 127.42	127.02
C1 (3)	G1	22	15	81	63	12	20	27	6	35	20	39	30	11
C2 (2)	G1	18	12	81	73	13	25	31	9	22	18	40	36	6
C3 (4)	G1	8.0	8.5	82	80	12	32	39	11	6	13	43	39	5
C4 (6)	G2	4.0	3.6	76	83	12	28	38	18	3	0.4	52	48	–
C5 (7)	G2	2.8	2.7	74	84	10	29	35	23	3	–	50	50	–



C^a



C^b

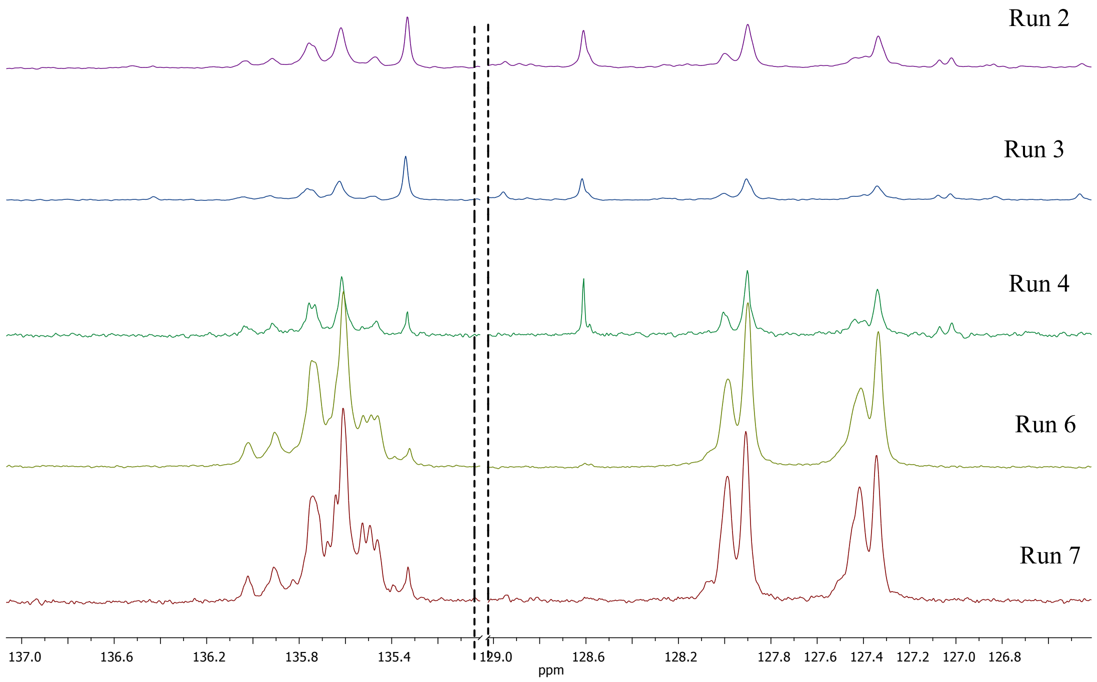


Figure S10. C=C double bond regions of COAc–NB (126.6–128.4 ppm) and NB–COAc (135.2–136.6 ppm) heterodyads in the ^{13}C NMR spectra of NB–COAc copolymers synthesized with the G1 and G2 catalysts (Run numbers from Table 2 are listed).

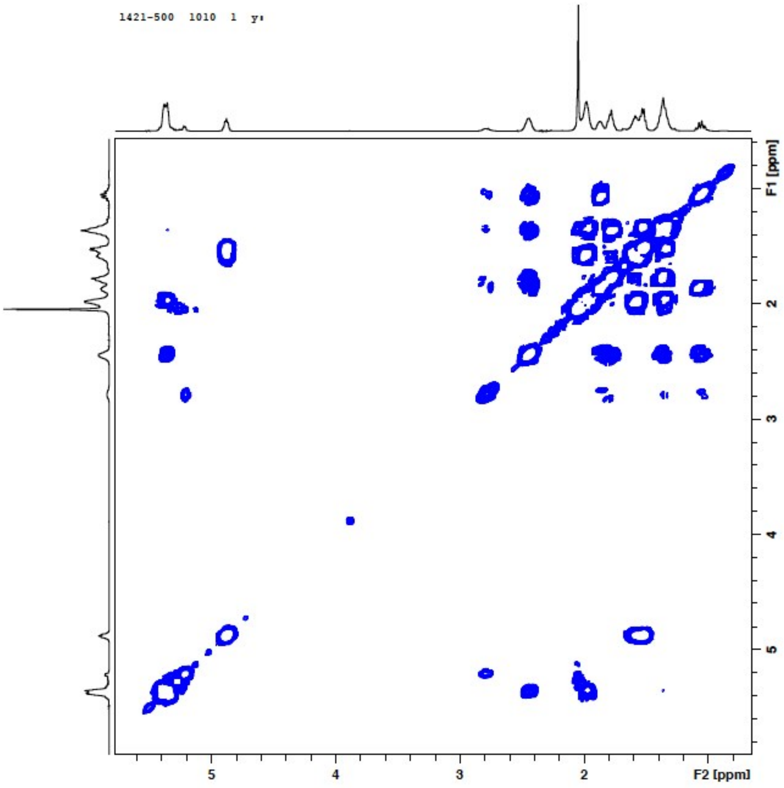


Figure S11. ${}^{1}H$–${}^{1}H$ COSY spectrum of NB−COAc multiblock copolymer at room temperature

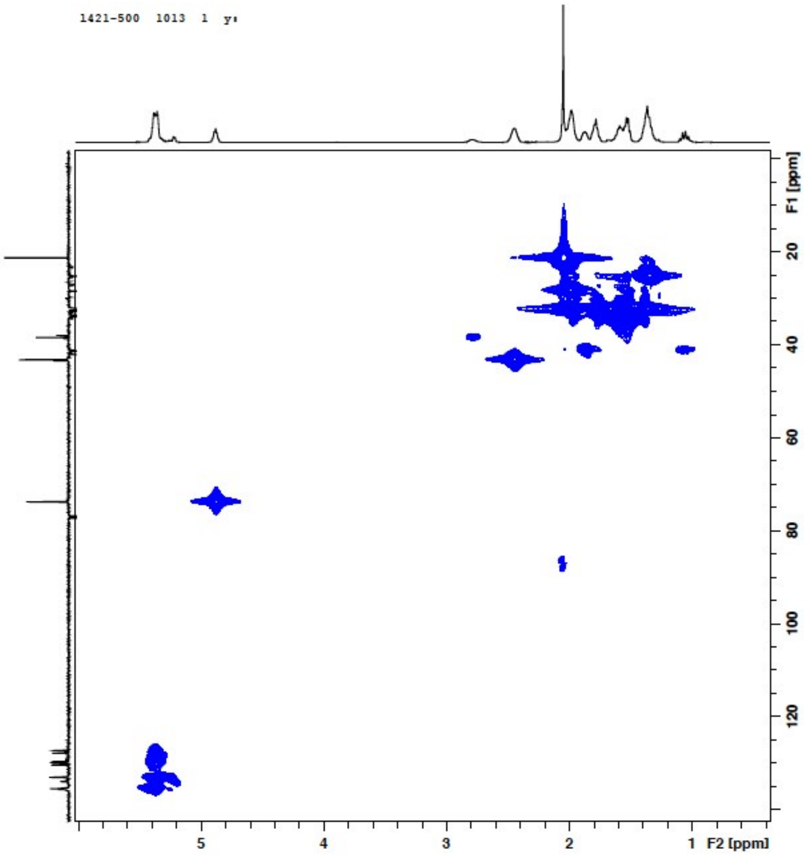


Figure S12. ${}^{1}H$– ${}^{13}C$ HMQC spectrum of NB−COAc multiblock copolymer at room temperature

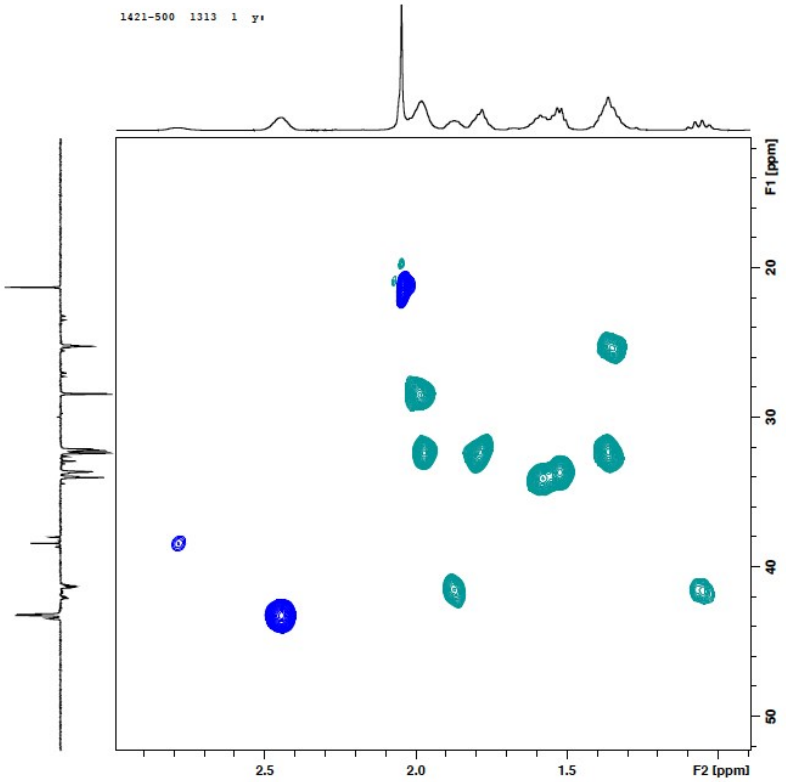


Figure S13. ^{1}H– ^{13}C HSQC (500MHz, $CDCl_3$, 50–0 ppm region of) spectrum of NB−COAc multiblock copolymer (room temperature)

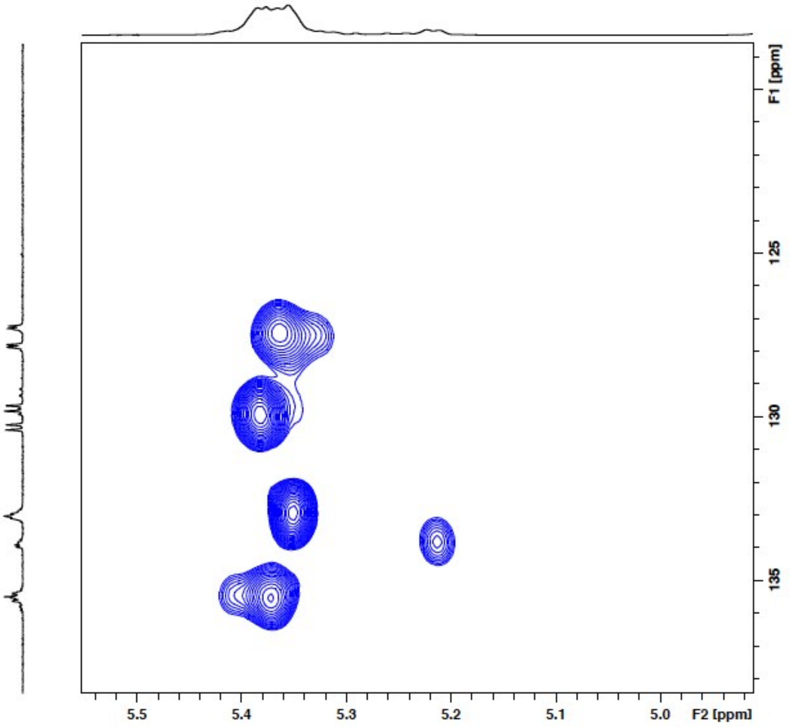


Figure S14. ^{1}H–^{13}C HSQC (500MHz, $CDCl_3$, 140–120 ppm region) spectrum of NB−COAc multiblock copolymer at room temperature

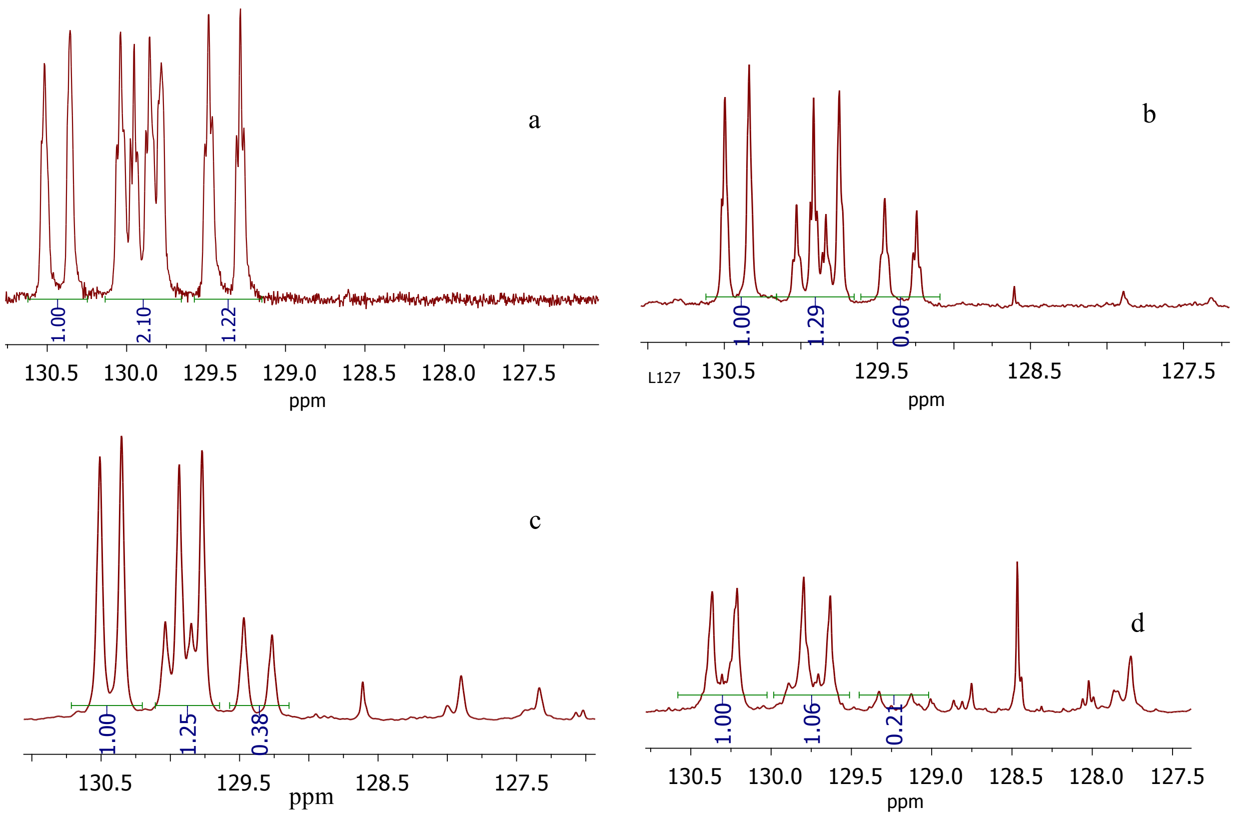


Figure S15. C=C double bond (in COAc units) region of the ^{13}C NMR spectrum (room temperature) in (a) homopolymer PCOAc and NB–COAc copolymers synthesized at different concentrations of the G1 catalyst (% mol): (b) 0.33, (c) 1, (d) 5

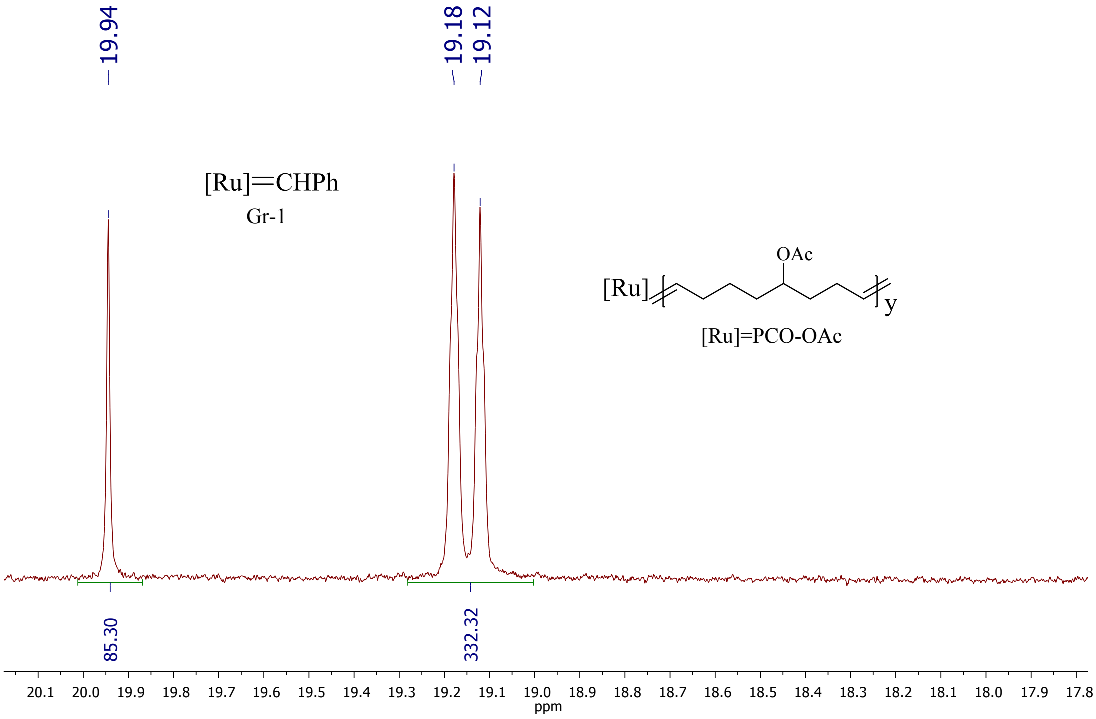


Figure S16. Carbene region of the ^{1}H NMR spectrum (room temperature) of PCOAc/G1 after 67 min of the reaction

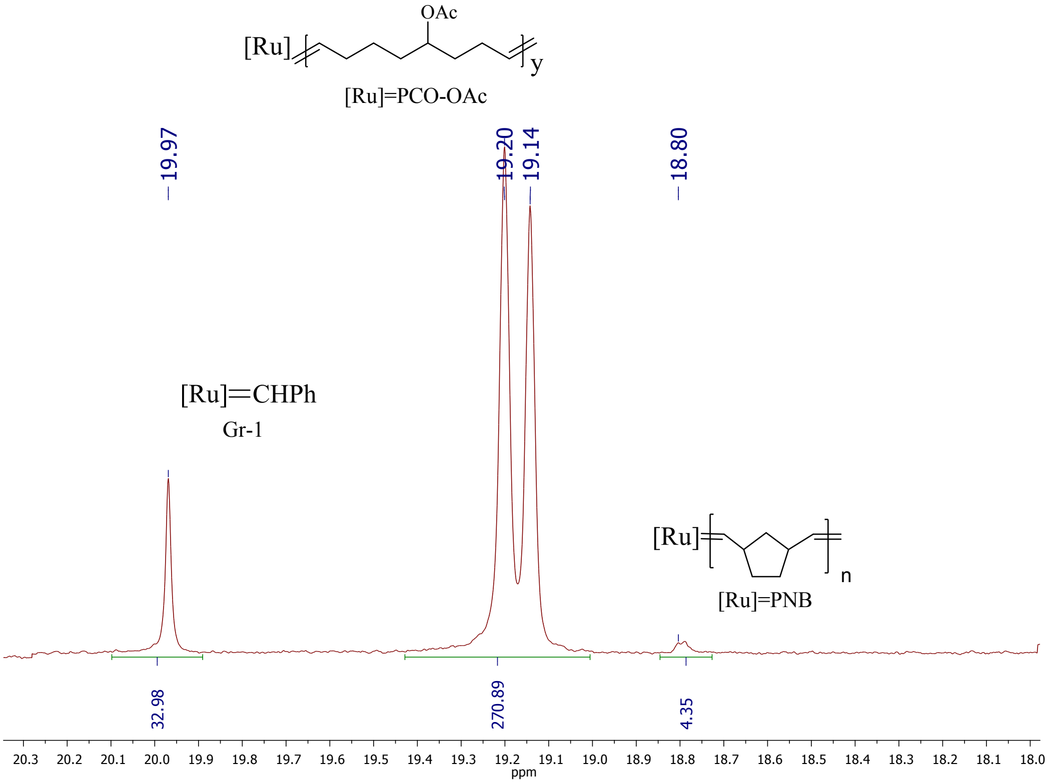


Figure S17. Carbene region of the ^{1}H NMR spectrum (room temperature) of PCOAc/PNB/G1 after 63 min of the reaction

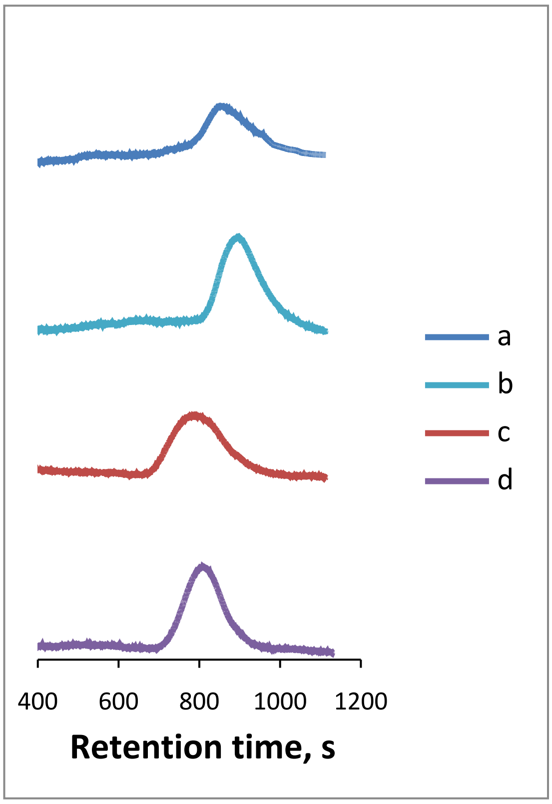


Figure S18. GPC curves of NB-COAc copolymers synthesized in presence of (a, Table 2, Run 4; b, Run 5) G1 and (c, Run 6; d, Run 7) G2 catalysts

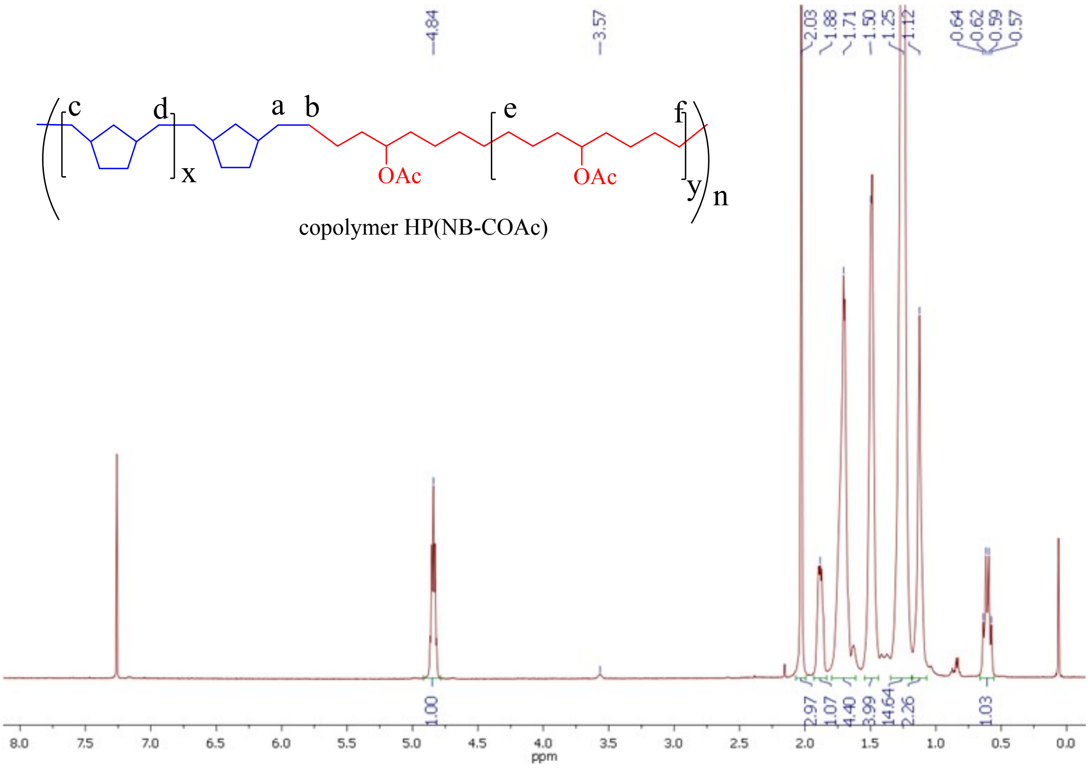


Figure S19. ^{1}H NMR spectrum of HP(NB–COAc) at room temperature

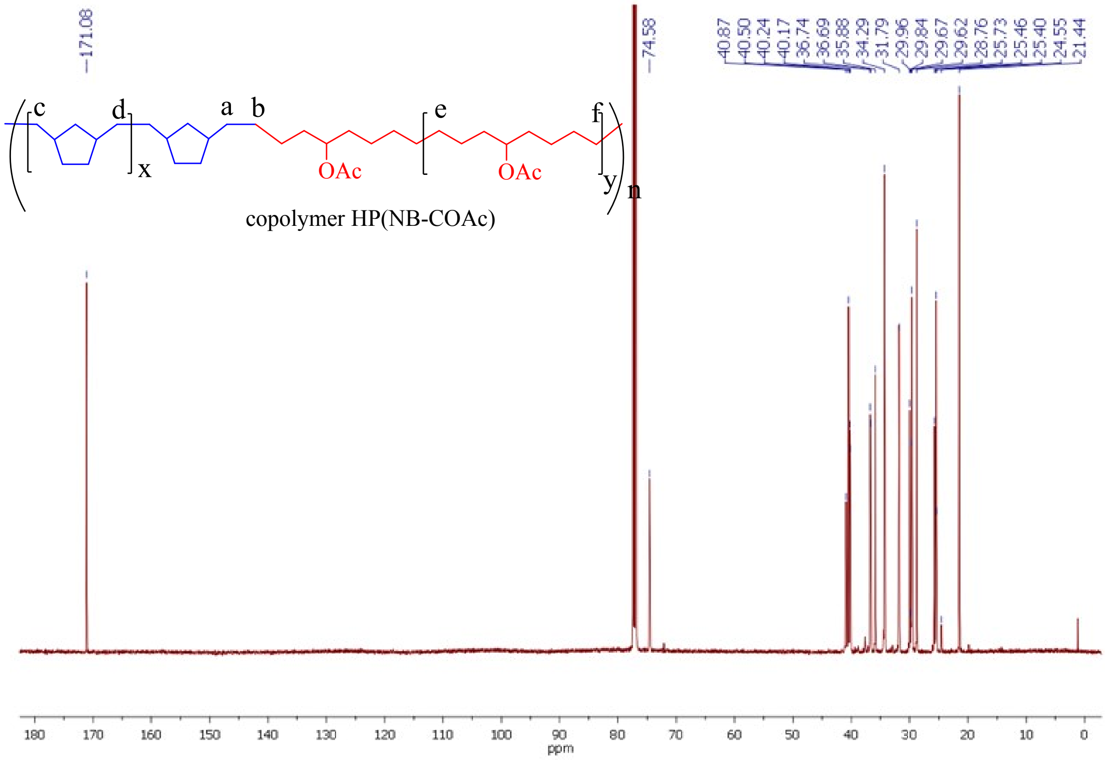


Figure S20. ^{13}C NMR spectrum of HP(NB–COAc) at room temperature

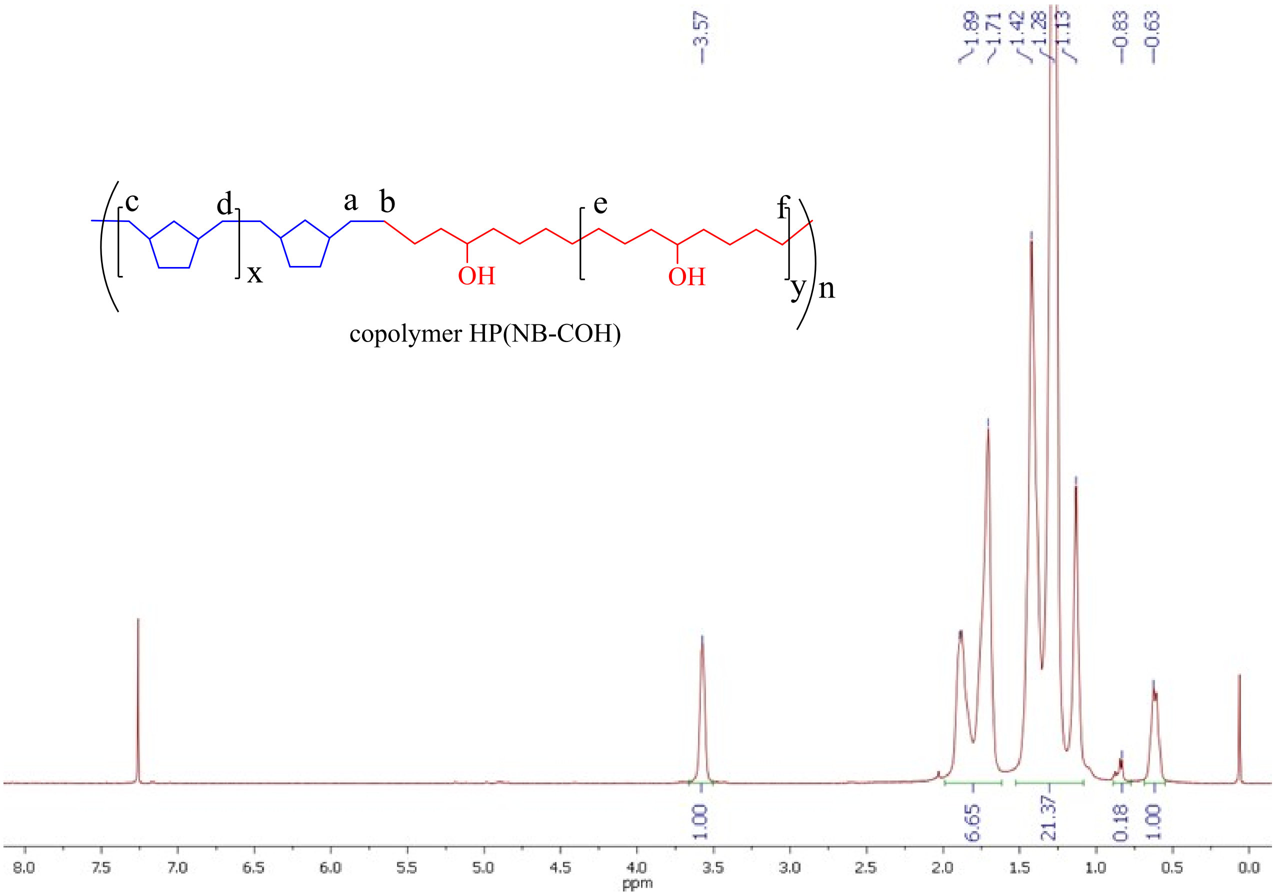


Figure S21. ^{1}H NMR spectrum of HP(NB–COH) at room temperature

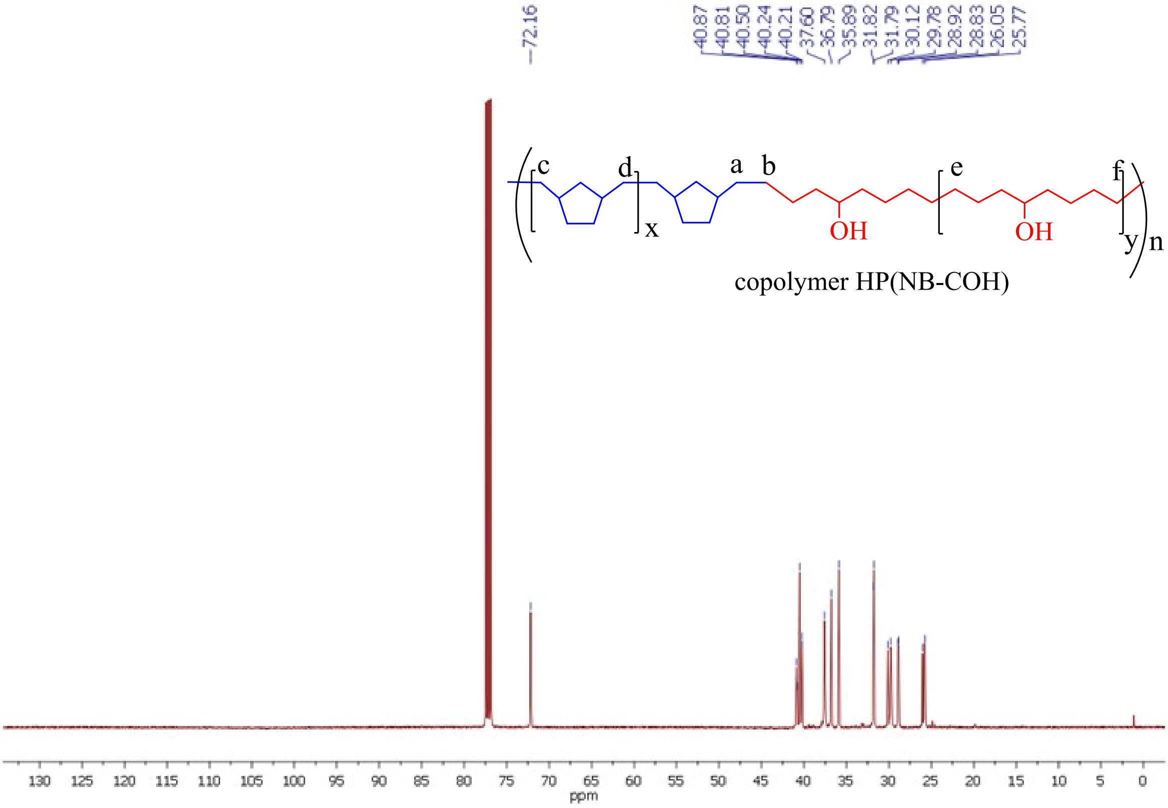


Figure S22. ^{13}C NMR spectrum of HP(NB–COH) at room temperature

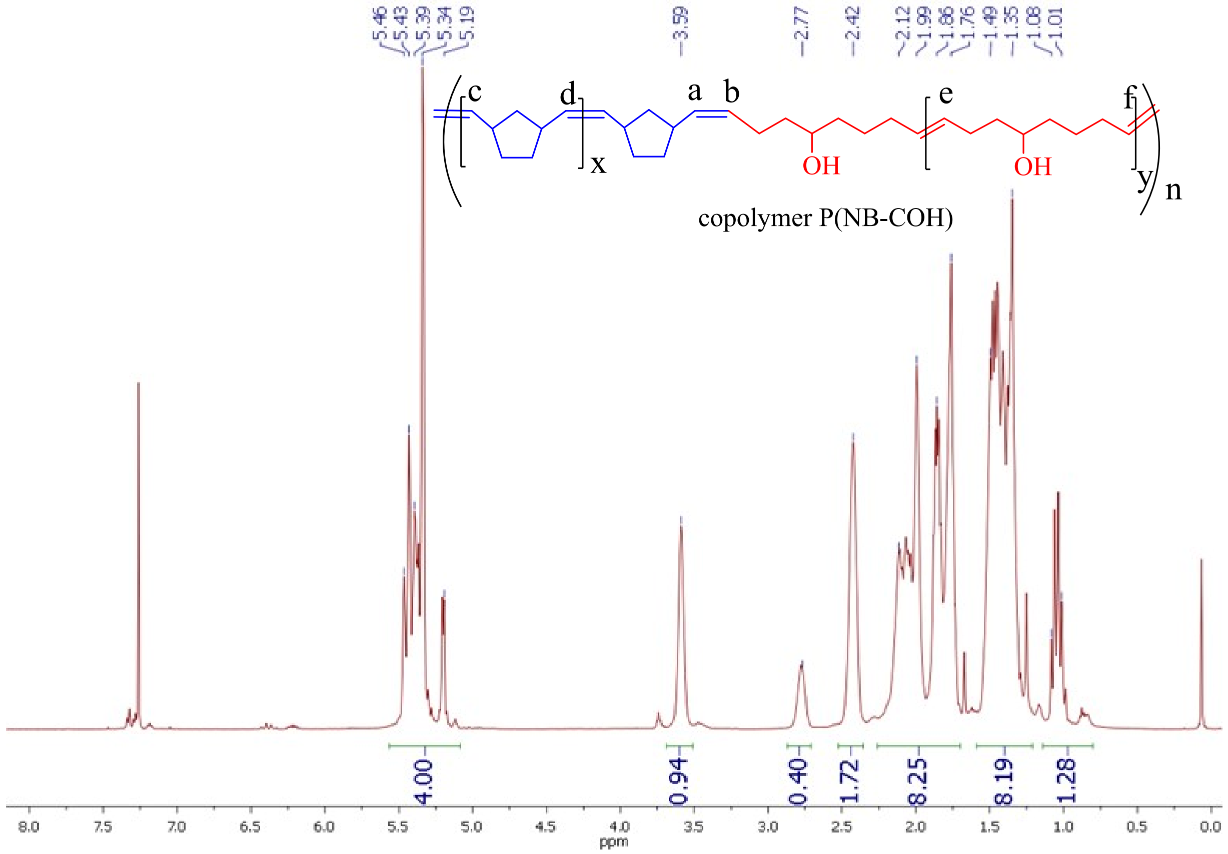


Figure S23. ^{1}H NMR spectrum of P(NB−COH) at room temperature

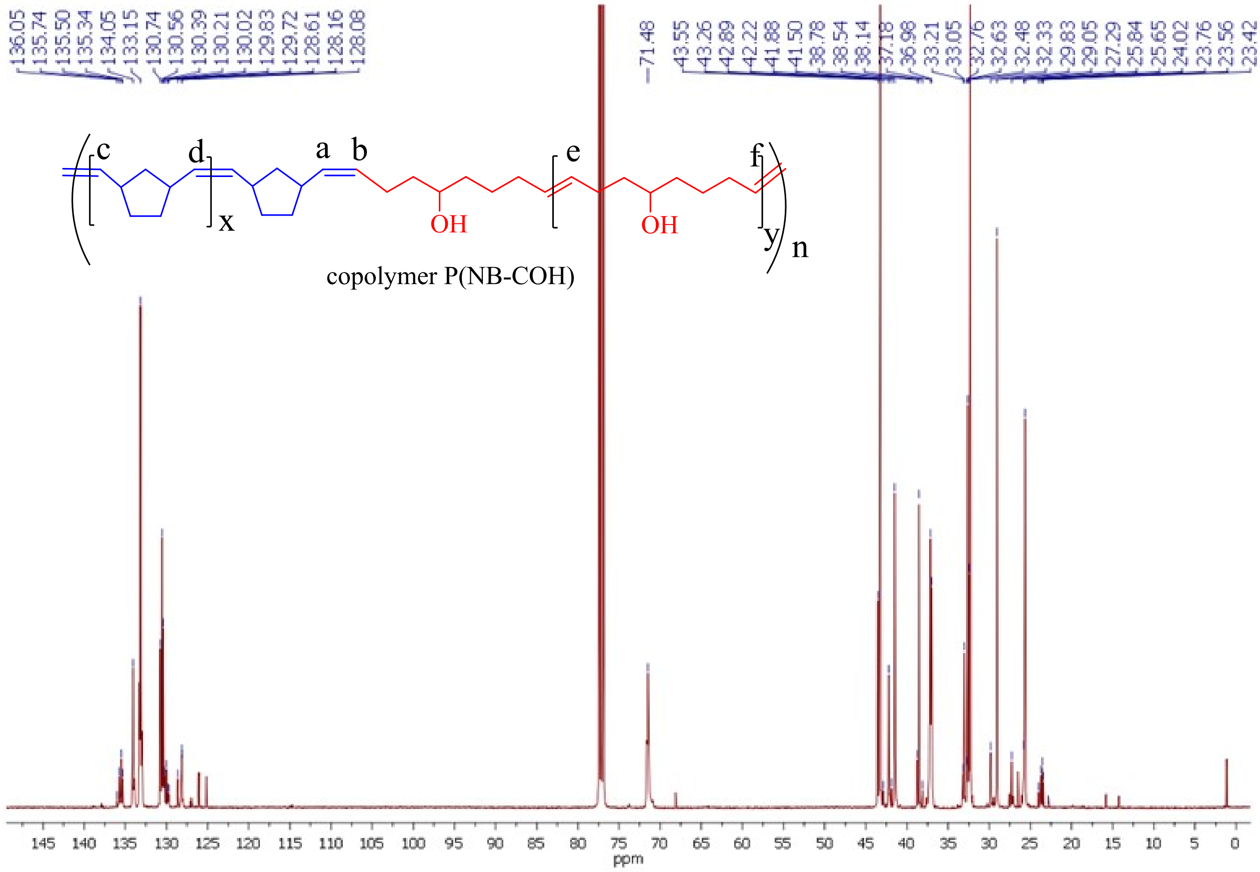


Figure S24. ^{13}C NMR spectrum of P(NB−COH) at room temperature

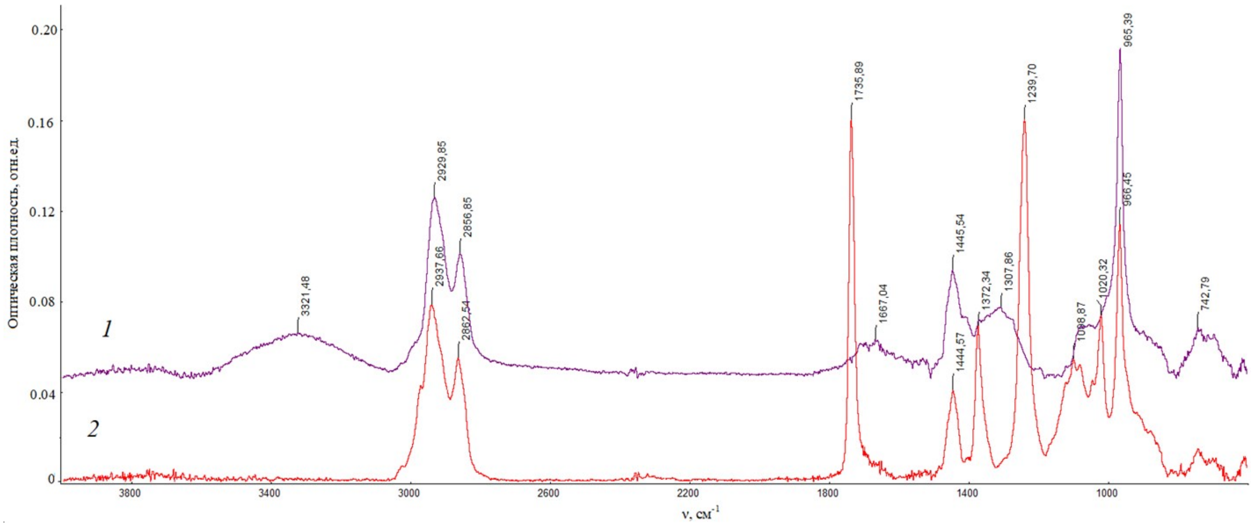


Figure S25. IR spectra of the (*1*) NB−COH and (*2*) NB−COAc copolymers

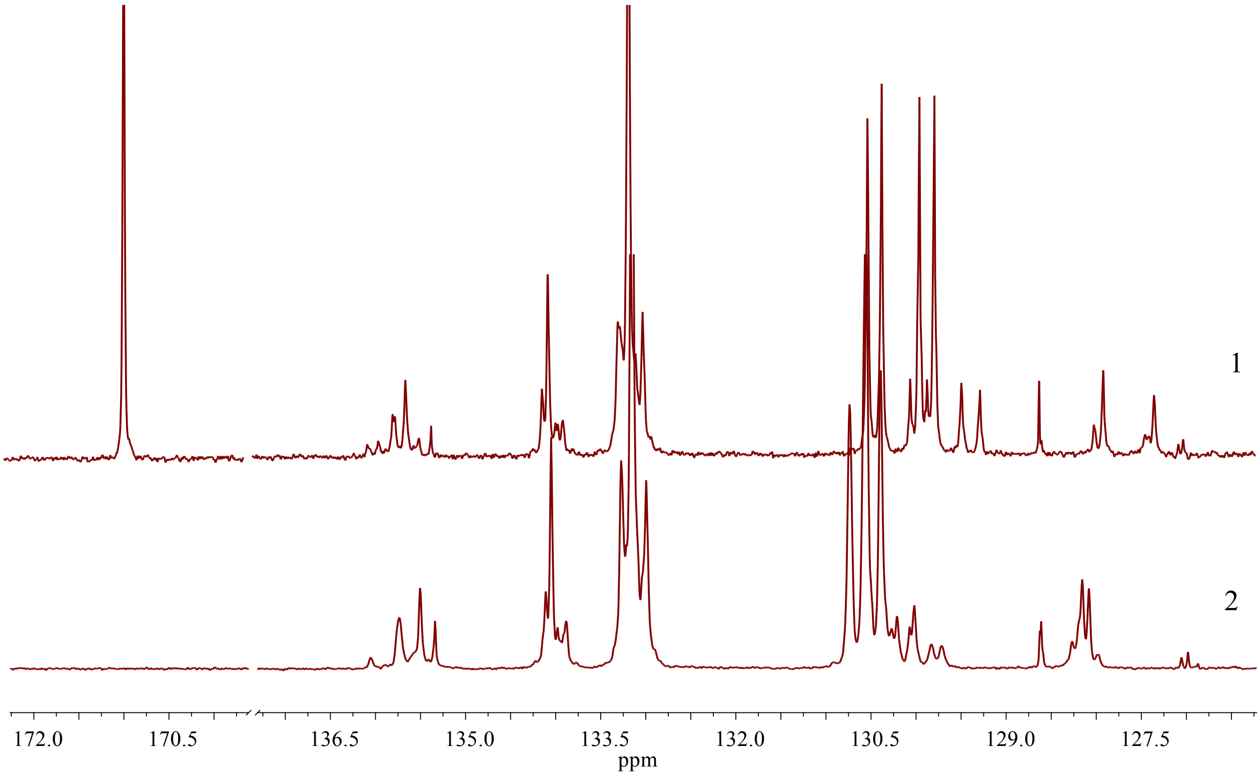


Figure S26. C=C double bond and carbonyl regions of the ^{13}C NMR spectra of (1) NB−COAc and (2) NB−COH copolymers at room temperature