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Novel copolymers for fibers based on cyclocarbonates and lactide

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Experimental Section

All reactions with air- and/or water-sensitive compounds were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. $CDCl_3$ (dried with CaH_2) was obtained from Deutero GmbH (Kastellaun, Germany). ^1H (400.13 MHz) and ^{13}C (100.61 MHz) NMR spectra were recorded on a Bruker Avance 400 (Bruker Corporation, Billerica, MS, USA) or Agilent 400-MR (Agilent Technologies, Santa Clara, CA, USA) spectrometers at room temperature (if otherwise stated). ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as internal standard. Elemental analysis was performed using EuroEA-3000 instrument (EuroVector, Pavia, Italy). Diethyl malonate, diethyl 2-ethylmalonate, tetrabutylammonium hydrogen sulfate, ethyl chloroformate, 1-iodobutane were used as purchased. Diethyl 2-butylmalonate was synthesized according to literature procedure.[S1]

Differential scanning calorimetry (DSC) were performed using a synchronous thermal analysis instrument STA 449 F3 Jupiter (Netzsch). Aluminum crucibles were used for the experiment, the sample weighed was 1–5 mg. The heating rate was 10 K min^{-1}; prior to the analysis, the baseline TGA and DSC was recorded.

The molecular weight characteristics of the polymers were studied by size exclusion chromatography (SEC). The SEC measurements were performed in THF at 35 °C with a flow rate of 0.9 ml min^{-1} using a Waters liquid chromatograph equipped with a refractive index detector (Waters R-410), and with three columns packed with Ultrastyragel with pore dimensions of 10^4 and 10^5 Å and a linear column (Waters Styragel® HR 5E for MW range 2000–4×10^6). The SEC system was calibrated using narrow dispersed linear polystyrene standards ranging from 800 to 2×10^6 g mol^{-1}.

Synthesis of diethyl 2-benzylmalonate [S2]

Metallic Na (0.6 g, 26.1 mmol) was dissolved in absolute ethanol (8 ml) placed in a 100 ml three-neck flask equipped with a magnetic stirrer, dropping funnel, and a reflux condenser with a calcium chloride tube. Diethyl malonate (8.0 g, 76.9 mmol) was added with vigorous stirring from a dropping funnel. After stirring for 10 min at room temperature, benzyl chloride (3.2 g, 25.0 mmol) was added dropwise. The reaction mixture was refluxed until the medium became neutral. After that, most of the ethyl alcohol was evaporated *in vacuo*, and then water was added to the oily residue and the mixture was extracted with ether (2x10 ml). The ether solution was dried over $MgSO_4$. The solution was concentrated on rotary evaporator and the product was purified by vacuum distillation (bp 168-170 °C, p = 15 Torr), yield: 4.2 g (85%), a pale-yellow oil.

^1H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.20 (6H, t, J = 7.1, CH_3), 3.22 (2H, d, J = 7.8, $PhCH_2$), 3.64 (1H, t, J = 7.8, CH), 4.14 (4H, q, J = 7.1, CH_2), 7.19-7.26 (5H, m, aromatic protons).

^{13}C NMR ($CDCl_3$, δ, ppm): 14.0 (CH_3), 34.7 ($PhCH_2$), 53.9 (CH), 61.4 ($O_2C\underline{C}H_2$), 126.7, 128.5, 128.8, 137.9 (aromatic carbons), 168.8 (C=O).

General procedure for 2-alkylpropane-1,3-diol synthesis

A solution of the corresponding diethyl malonate (1 eq.) in THF was added dropwise to a suspension of $LiAlH_4$ (3.0 eq.) in THF in an inert atmosphere, and then left to stir overnight at room temperature. Water was added dropwise to neutralize the excess of $LiAlH_4$, after which 15% NaOH solution and water were added, then stirred for 30 min. The reaction mixture was diluted with ethyl acetate, the precipitate that formed was filtered off on a Buchner funnel, the precipitate was washed with ethyl acetate, and the organic extracts were combined. The solution was dried over Na_2SO_4, the solvent was removed under reduced pressure.

2-Benzylpropane-1,3-diol [S3]: The product was obtained as white crystals. m.p. 68-70 ° C (88%). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 2.04 (1H, m, CH); 2.59 (2H, d, J = 7.6, $PhCH_2$); 2.87 (2H, s, OH); 3.63 (2H, m, CH_2); 3.75 (2H, m, CH_2); 7.16-7.29 (5H, m, aromatic protons).^{13}C NMR ($CDCl_3$, δ, ppm): 34.19 ($PhCH_2$); 43.77 (CH); 65.23 (OCH_2); 126.09; 128.40; 128.94; 139.79 (aromatic carbons).

2-Butylpropane-1,3-diol [S4]: A pale-yellow oil was obtained (yield 74%).^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.85 (3H, t, J = 6.8, CH_3); 1.17-1.27 (6H, m, CH_2CH_2 CH_2); 1.68 (1H, m, CH); 3.56 (2H, m, CH_2); 3.71 (2H, m, CH_2).^{13}C NMR ($CDCl_3$, δ, ppm): 13.91 (CH_3); 22.86 (CH_2); 27.38 (CH_2); 29.30 (CH_2); 41.87 (CH); 65.59 (OCH_2).

2-Ethylpropane-1,3-diol [S3]: A pale-yellow oil was obtained (yield 81%). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, t, J = 7.5, CH_3); 1.23 (2H, quint, J = 7.3, CH_2); 1.59 (1H, m, CH); 3.56 (2H, m, CH_2); 3.71 (2H, m, CH_2); 3.81 (2H, br.s., OH).^{13}C NMR ($CDCl_3$, δ, ppm): 11.58 (CH_3); 20.51 (CH_2); 43.57 (CH); 65.17 (OCH_2).

General procedure for the cyclocarbonate synthesis

Triethylamine (3.2 eq.) was added dropwise to a mixture of the corresponding 1,3-diol (1.0 eq) and ethyl chloroformate (3.0 eq.) dissolved in THF at 0 °C for 30 min. The reaction mixture was stirred at room temperature for 2 h. The precipitated triethylamine hydrochloride was filtered off and the solvent was removed under reduced pressure.

5-Benzyl-1,3-dioxan-2-one (**3**): The residue was recrystallized from THF and ether. A white solid was obtained. The product yield was 72%. m.p. 72-74 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 2.48 (1H, m, CH); 2.73 (2H, d, J = 7.8, $PhCH_2$); 4.17 (2H, m, CH_aH_b); 4.39 (2H, m, CH_aH_b); 7.15-7.35 (5H, m, aromatic protons). ^{13}C NMR ($CDCl_3$, δ, ppm): 32.75 ($Ph\underline{C}H_2$); 33.63 (CH); 71.40 (OCH_2); 127.02; 128.62; 128.90; 136.68 (aromatic carbons); 148.35 (C=O). Anal. Calcd for (%) $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found (%): C, 68.54; H, 6.11.

5-Butyl-1,3-dioxan-2-one (**2**): The volatile components was removed *in vacuo* (temperature of oil bath was 100 °C, p = 2 mbar). The product was obtained as a yellow oil (99%). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.85 (3H, m, CH_3); 1.22-1.36 (6H, m, CH_2CH_2 CH_2); 2.17 (1H, m, CH);

4.06 (2H, m, CH_aH_b); 4.39 (2H, m, CH_aH_b). ^{13}C NMR ($CDCl_3$, δ, ppm.): 13.67 (CH_3); 22.45 (CH_2); 26.83 (CH_2); 28.55 (CH_2); 31.08 (CH); 72.03 (OCH_2); 148.57 (C=O).

5-Ethyl-1,3-dioxan-2-one (**1**): The volatile components was removed *in vacuo* (temperature of oil bath was 100 °C, p = 2 mbar). The product was obtained as a yellow oil (82%). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.95 (3H, t, J = 7.6, CH_3); 1.38 (2H, quint, J = 7.6, CH_2); 2.09 (1H, m, CH); 4.06 (2H, m, CH_aH_b); 4.39 (2H, m, CH_aH_b).^{13}C NMR ($CDCl_3$, δ, ppm): 10.99 (CH_3); 20.35 (CH_2); 32.59 (CH); 71.81 (OCH_2); 148.57 (C=O).

2.5. General procedure of homopolymers and copolymers synthesis

Initiator (1.0 M solution $ZnEt_2$ in hexanes) was added to the corresponding trimethylene carbonate **1-3** (trimethylene carbonate and L-lactide) in an inert atmosphere. The reaction mixture was heated at 100 °C for 3-90 h. The conversion was monitored by using ^{1}H NMR spectroscopy. Then, methanol was added to the reaction mixture. The solvents were removed *in vacuo*. Dichloromethane was added to the dry residue until complete dissolution. The resulting solution was poured into methanol with vigorous stirring. The precipitated polymer was separated and dried in a vacuum.

Homopolymer of BnTMC **(P3)**. The general procedure described above was followed using BnTMC and $ZnEt_2$ (initiator) with molar ratio 500:1, T = 100° C, t = 1 h, yield = 81%.^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 2.35 (1H, m, CH); 2.70 (2H, m, $PhCH_2$); 4.00-4.20 (4H, m, CH_2); 7.11-7.35 (5H, m, aromatic protons).

Homopolymer of BuTMC **(P2).** The general procedure described above was followed using BnTMC and $ZnEt_2$ (initiator) with molar ratio 500:1, T = 100° C, t = 48 h, yield 91%. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.87 (3H, m, CH_3); 1.22-1.36 (6H, m, CH_2CH_2 CH_2); 2.03 (1H, m, CH); 4.04-4.23 (4H, m, CH_2).

Homopolymer of EtTMC **(P1).** The general procedure described above was followed using EtTMC and $ZnEt_2$ (initiator) with molar ratio 500:1, T = 100° C, t = 48 h, yield 74%. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.94 (3H, t, J = 7.5, CH_3); 1.42 (2H, m, CH_2); 1.95 (1H, m, CH); 4.10-4.20 (4H, m, CH_2).

Copolymers. The general procedure described above was followed using corresponding trimethylene carbonate **1-3** and L-lactide (in molar ratio LA : RTMC : $ZnEt_2$=500:500:1 or 500:50:1). Yields were 45%-90%.

Additional figures and tables

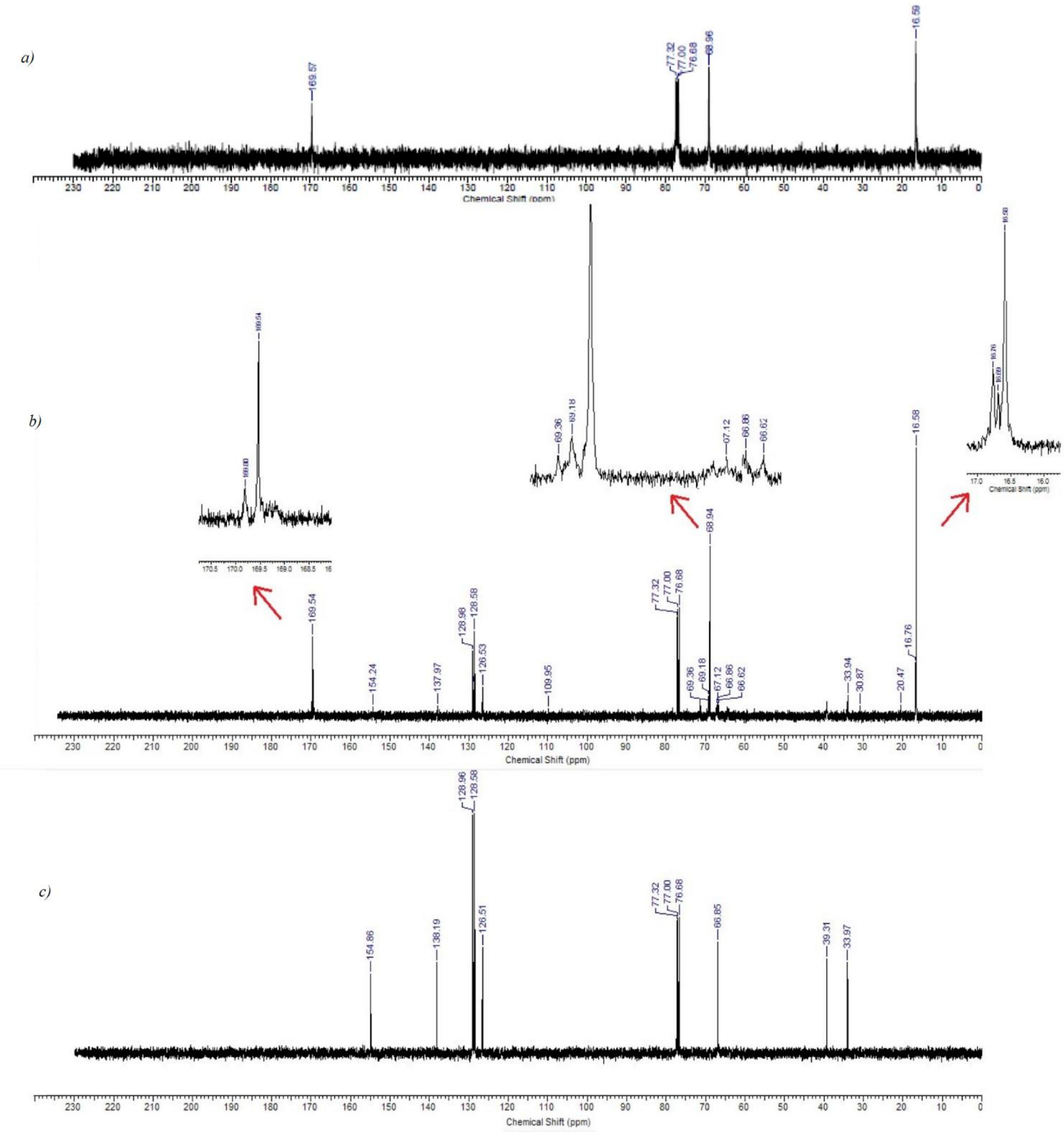


Figure S1 *a)* ^{13}C-NMR spectra of homo-poly-LA, *b)* copolymer of LA and BnTMC (ratio 75/25) **(CP7)**, *c)* homo-poly-BnTMC **(P3)**.

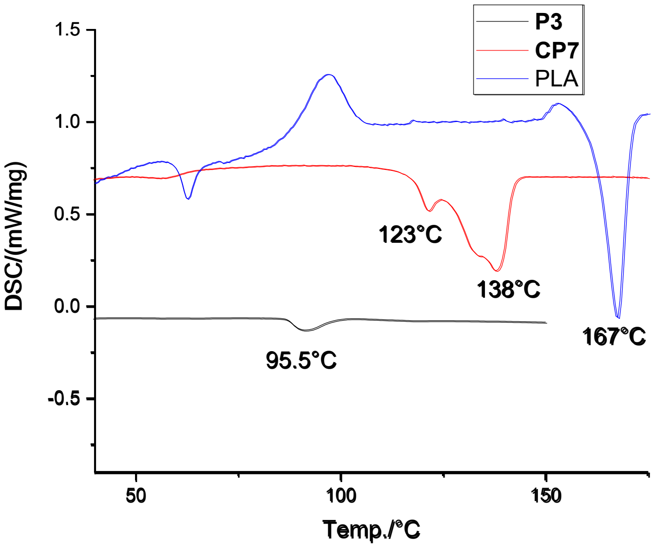


Figure S2 DSC thermograms of homo-poly-L-lactide (PLA-6252D, M_w=97 kDa, PDI=1.5), homo- poly(benzyltrimethylene carbonate) **P3** and their 75/25 copolymer **CP7**. (Hereinafter: samples of all polymers for DSC were preliminarily kept for an hour at a temperature of 60°C).

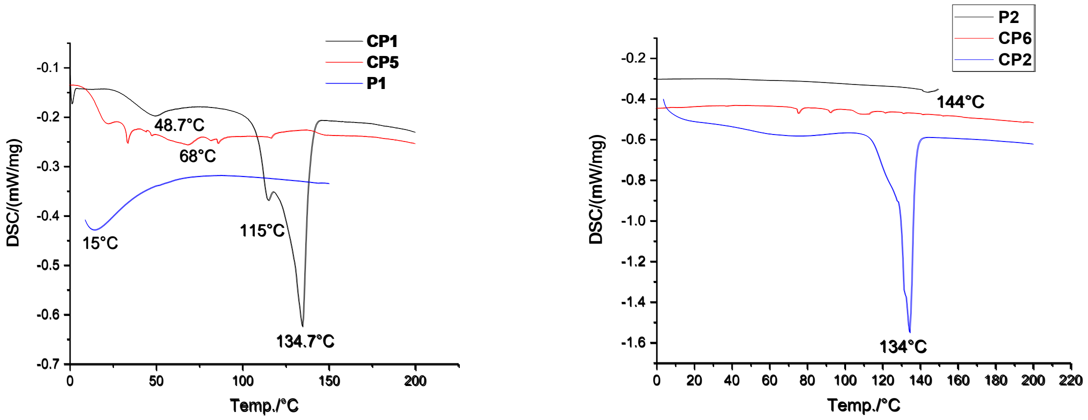
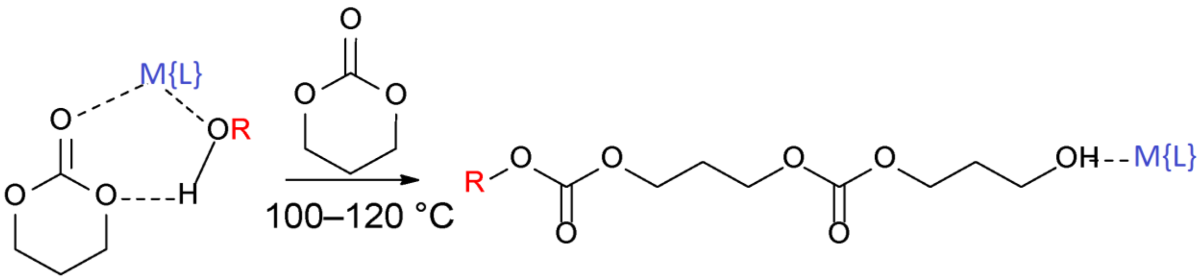

(*a*) (*b*)

Figure S3 DSC thermograms of polymers based on ethyltrimethylene carbonate **P1, CP1, CP5** (*a*) and butyltrimethylene carbonate **P2, CP2, CP6** (*b*)

Table S1 Mechanical properties of mixed composition samples

Sample	Yield strength, MPa	Tensile strength, MPa	Elongation at break, %
S1 (PLA6252D : [LA(80%) - (**EtTMC**) (20%) copolymer (sample **CP5**, Table 2)] = 9:1)	35.6 ±6.5	33.6 ±5.2	4.2±0.3
S2 (PLA6252D: poly**EtTMC** = 9:1)	48.9±6.4	44.1±3.3	4.4±0.3
S3 (PLA6252D : [LA(75%)-(**BnTMC**) (25%) copolymer (sample **CP7**, Table 2)] = 9:1)	44.3±5.2	36.9±5.5	3.7±0.6
S4 (PLA6252D:poly**BnTMC**) = 9:1)	48.7±4.6	40.1±4.6	4.0±0.3
Control (PLA6252D without additives)	55.1±3.6	46.3±19.3	5.9±0.2



Scheme S1. Coordination-insertion mechanism in the presence of external nucleophile.

Spectra of compounds

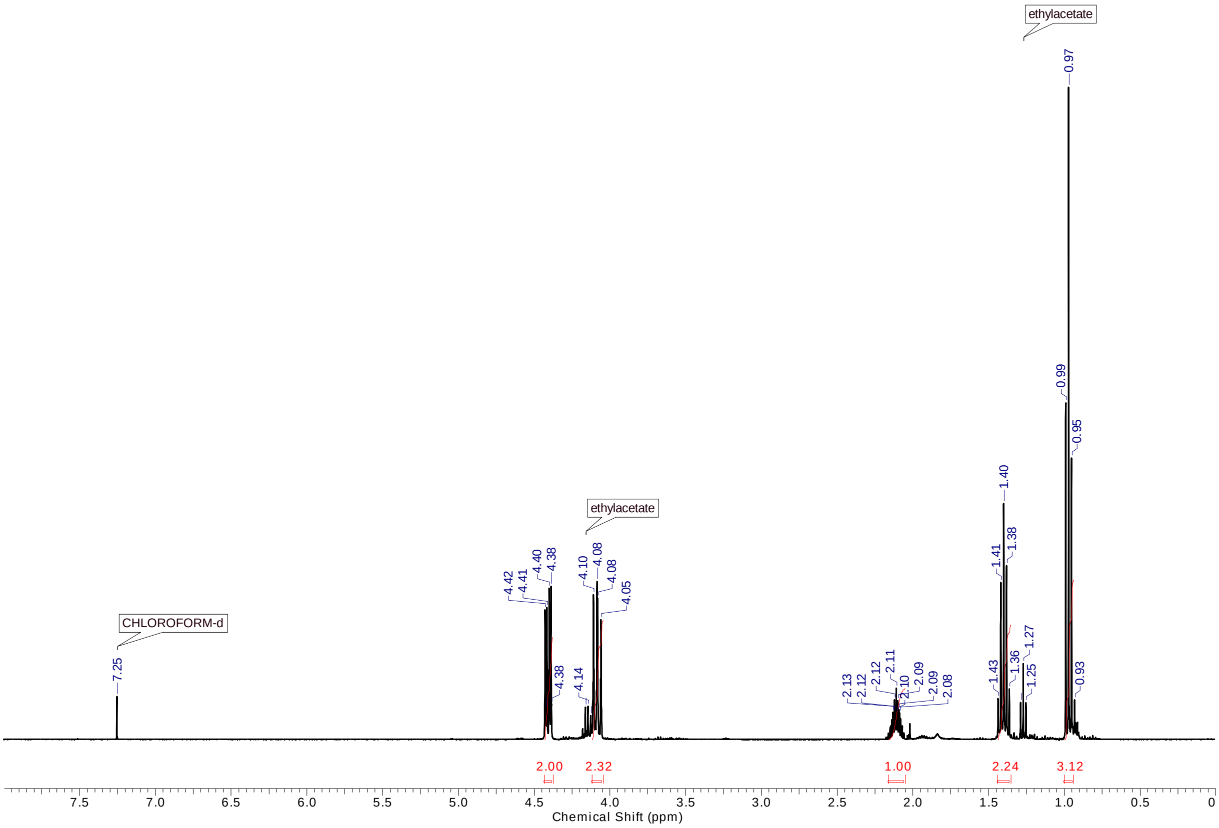


Figure S4.^{1}H NMR spectrum of 5-ethyl-1,3-dioxan-2-one **1**

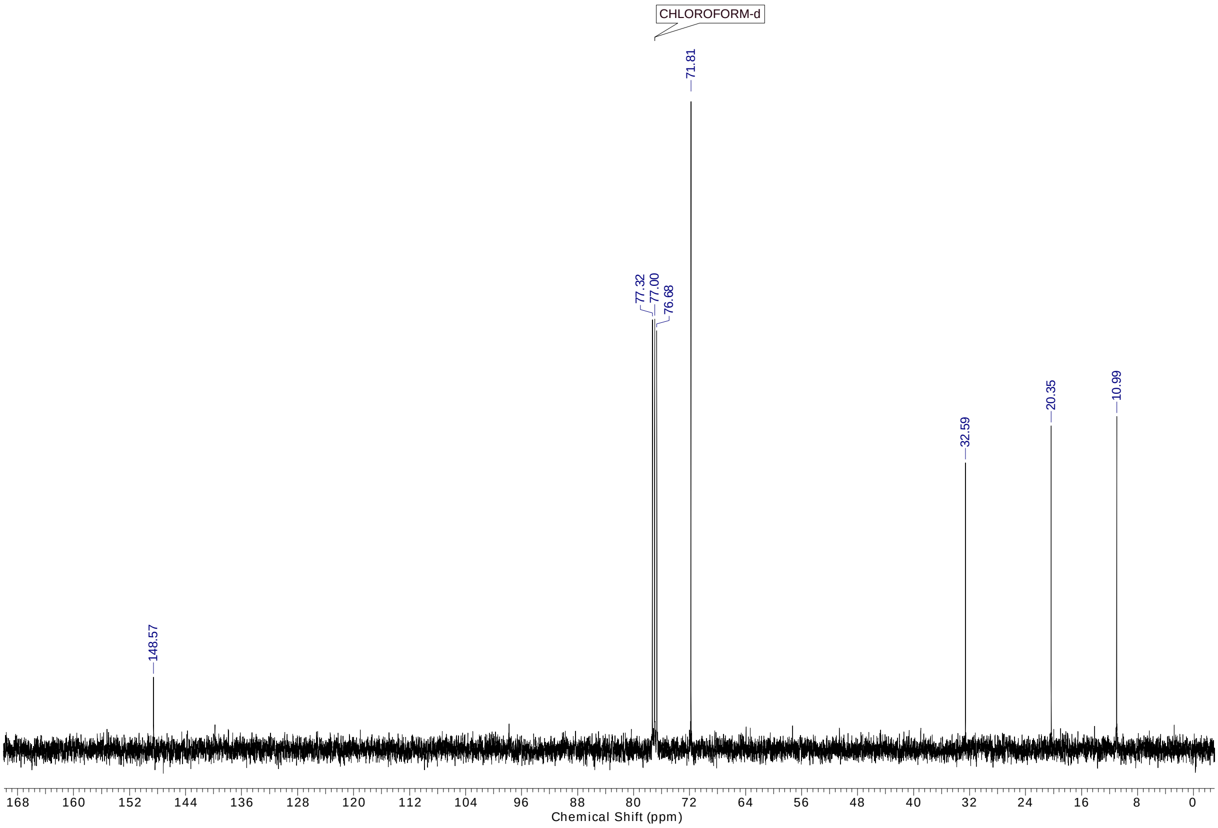


Figure S5.^{13}C NMR spectrum of 5-ethyl-1,3-dioxan-2-one **1**

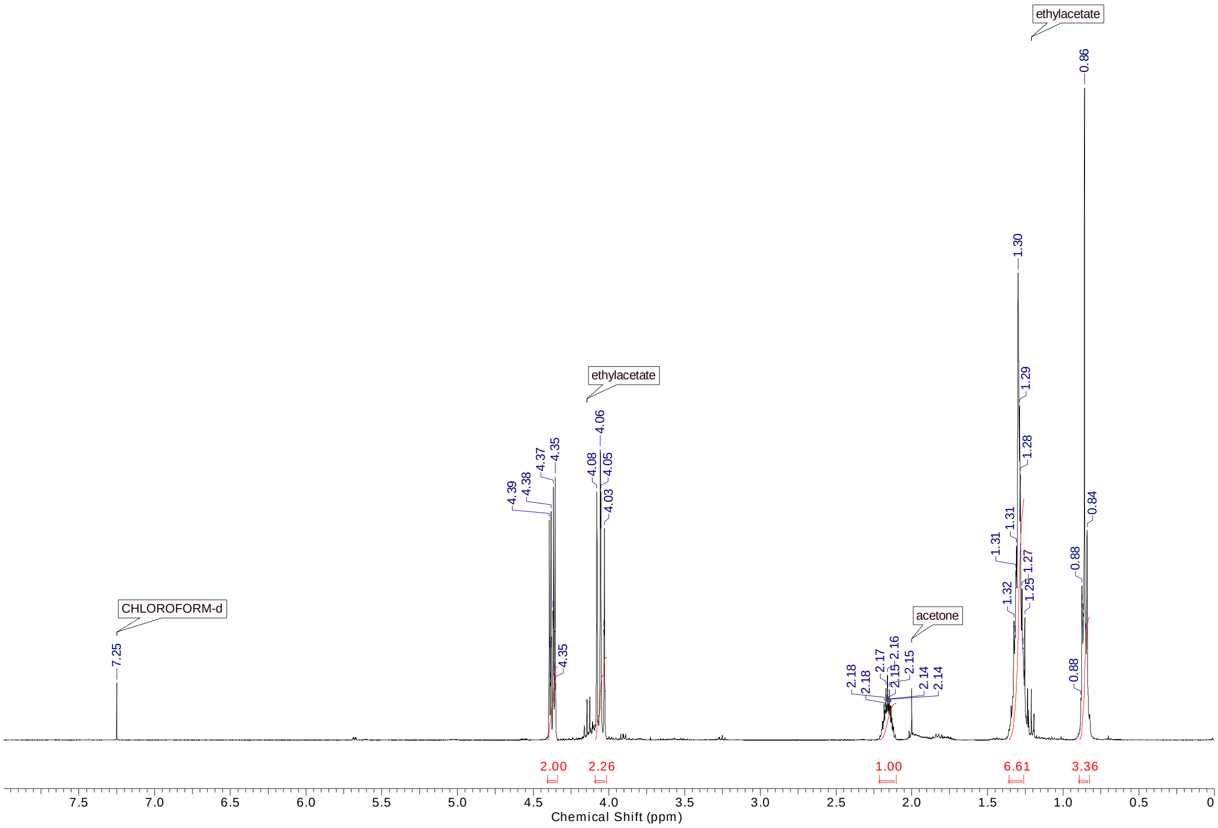


Figure S6. ^{1}H NMR spectrum of 5-butyl-1,3-dioxan-2-one **2**

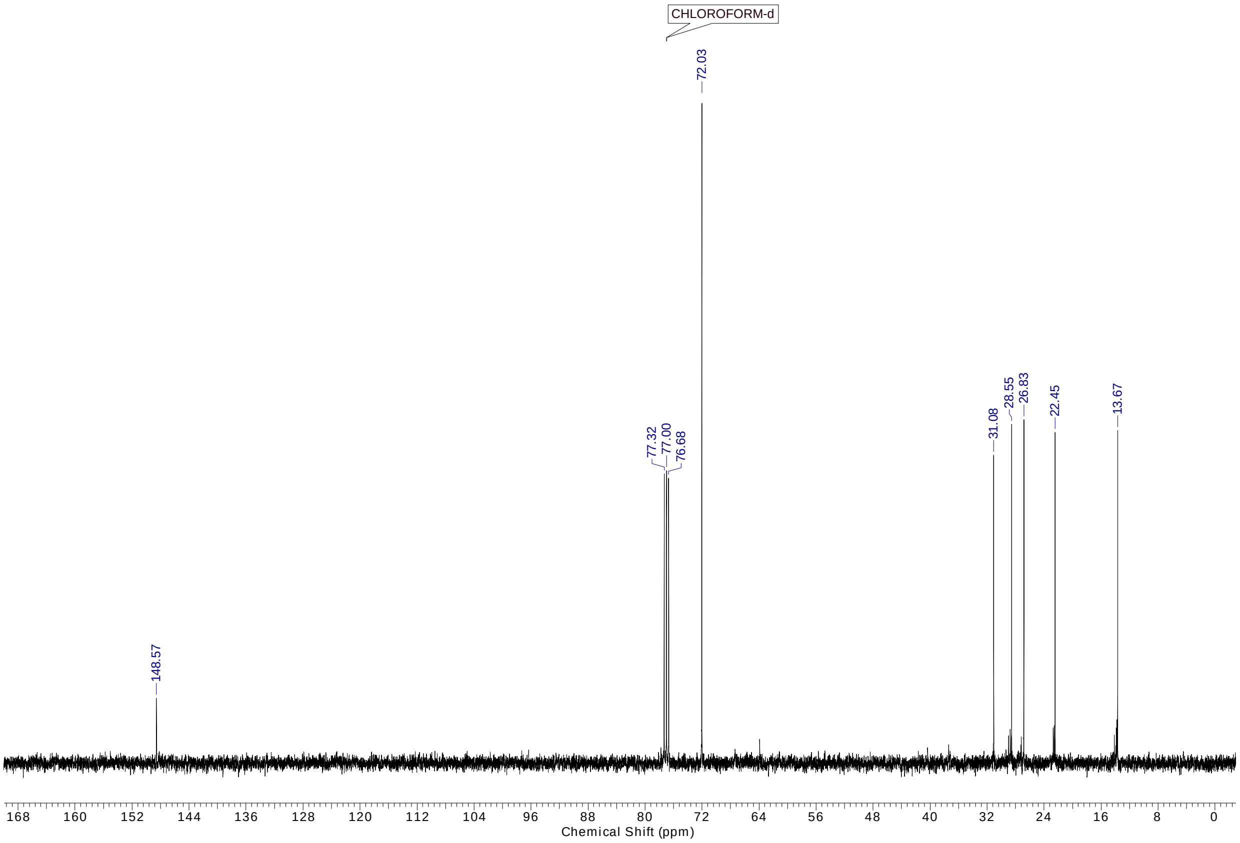


Figure S7. ^{13}C NMR spectrum of 5-butyl-1,3-dioxan-2-one **2**

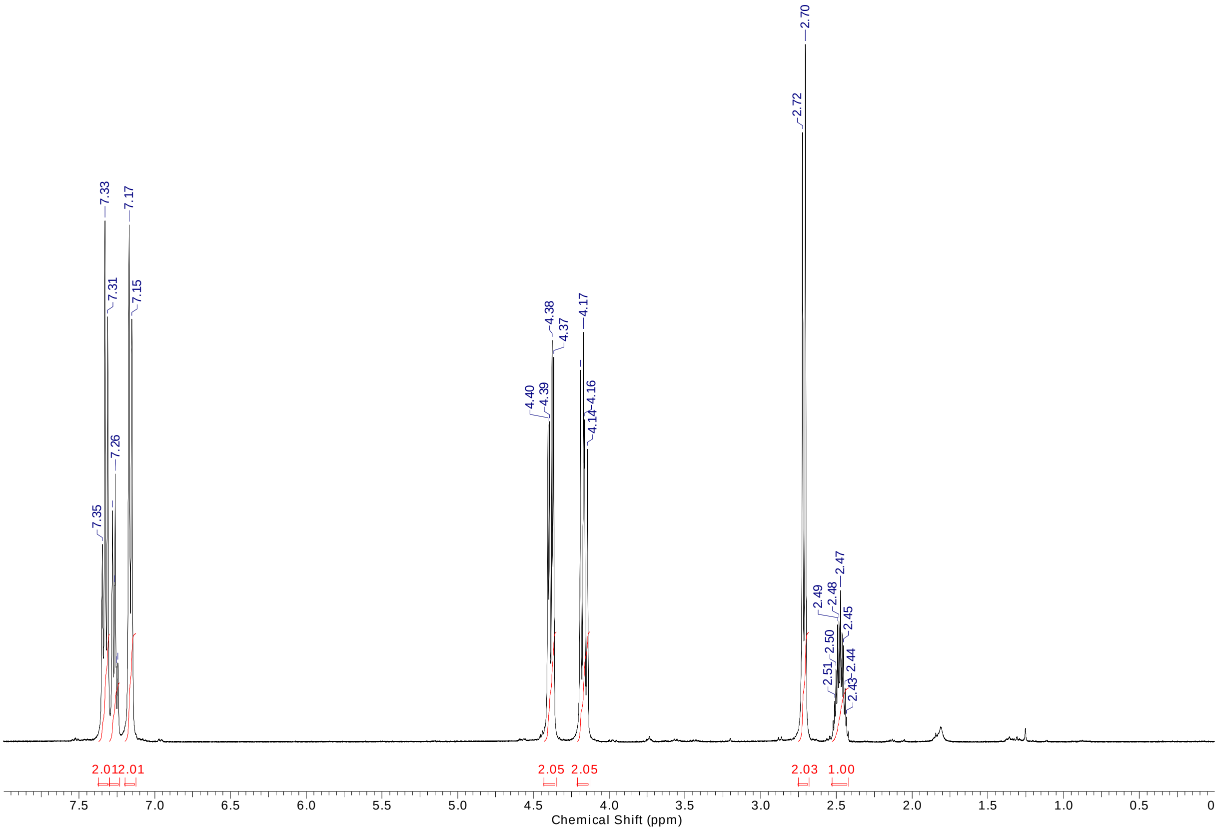


Figure S8. ^{1}H NMR spectrum of 5-benzyl-1,3-dioxan-2-one **3**

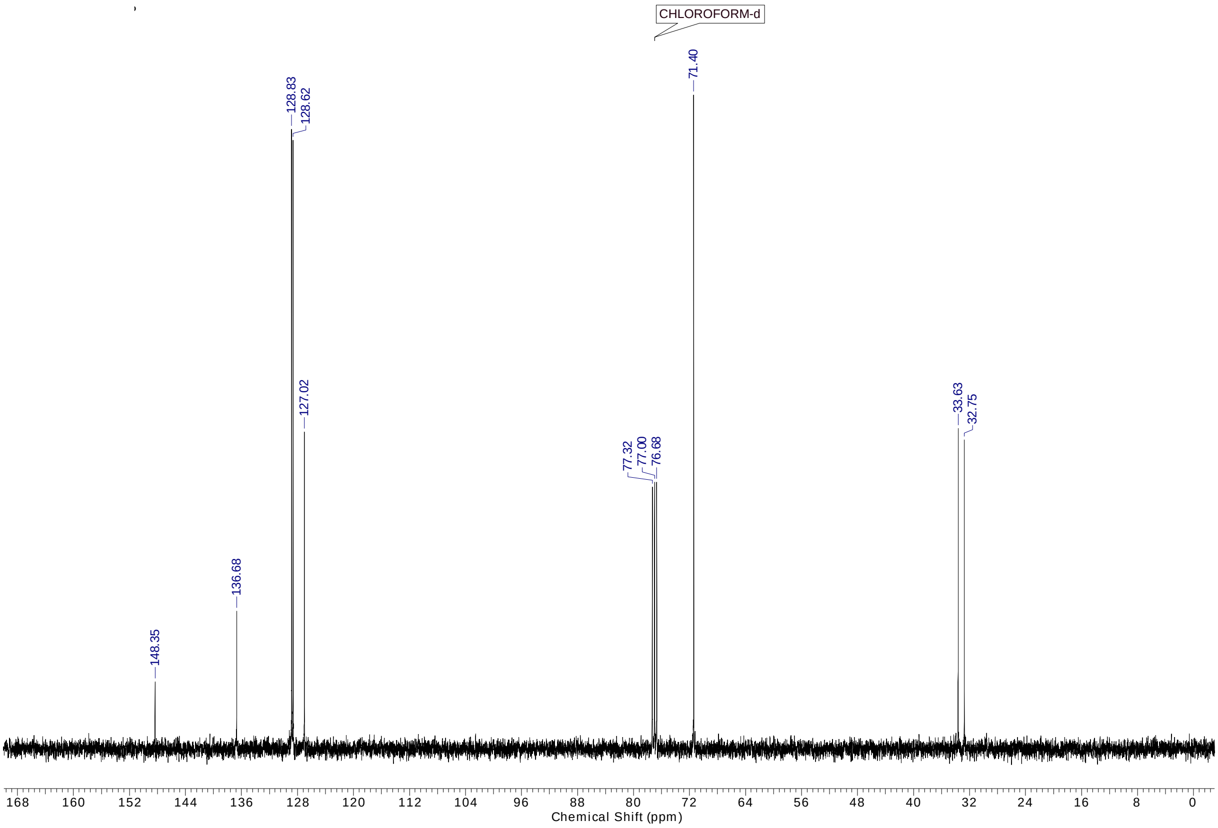


Figure S9. ^{13}C NMR spectrum of 5-benzyl-1,3-dioxan-2-one **3**

Spectra of polymers

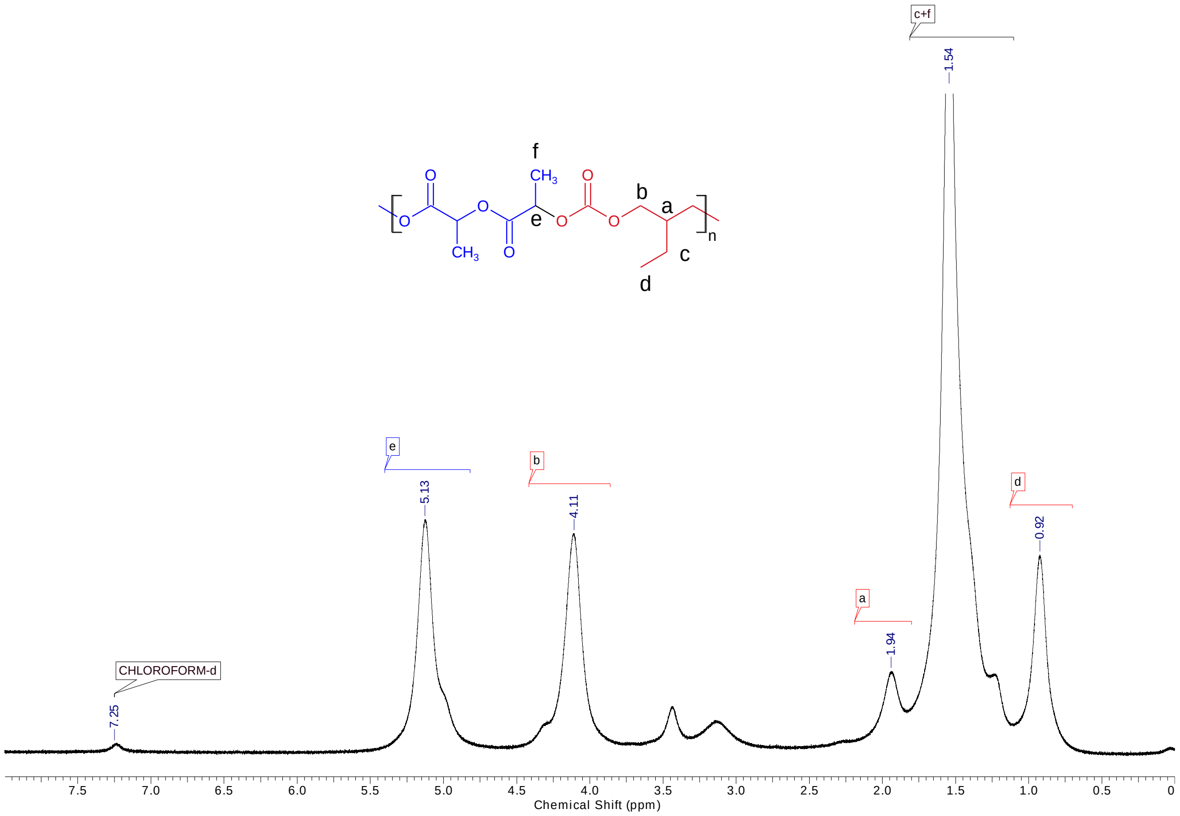


Figure S10.^{1}H NMR spectrum of copolymer of LA and EtTMC **CP5**

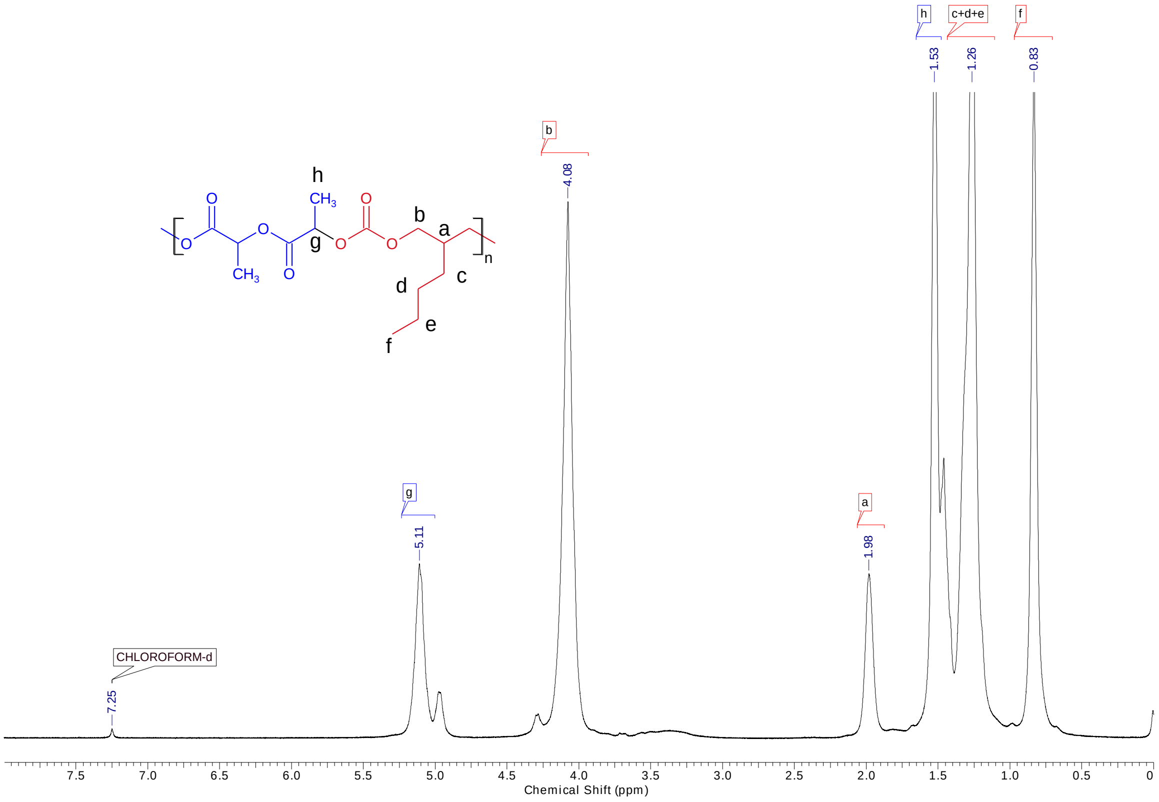


Figure S11.^{1}H NMR spectrum of copolymer of LA and BuTMC **CP5**

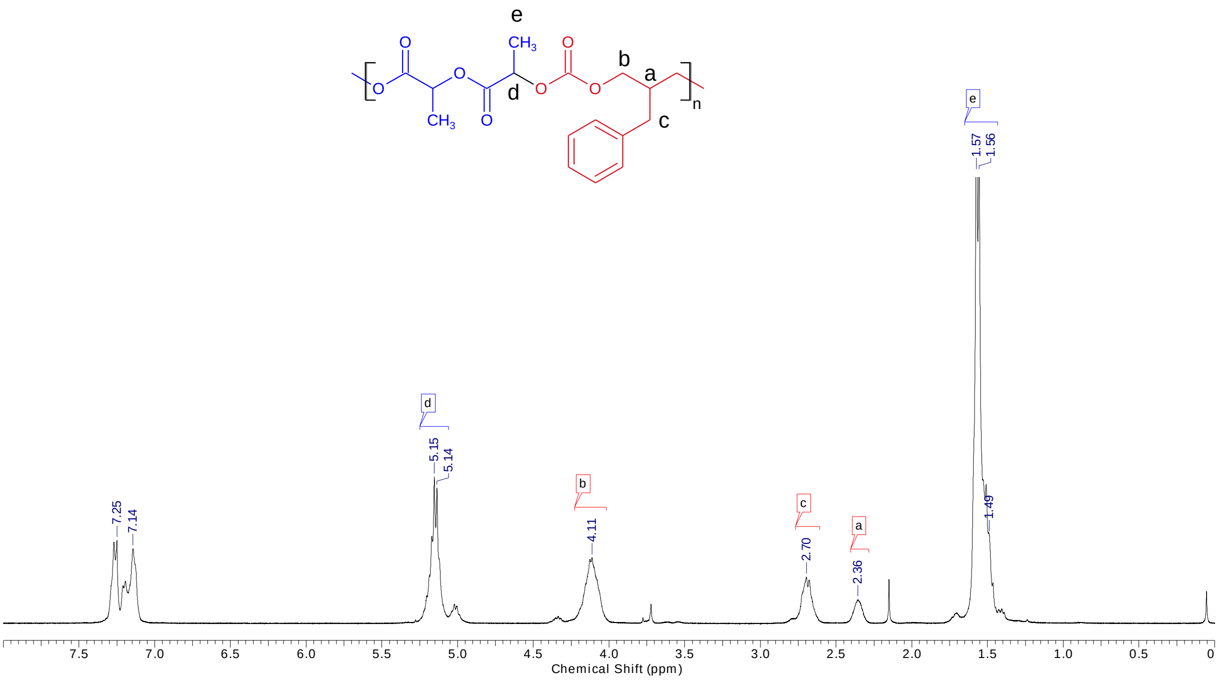


Figure S12.^{1}H NMR spectrum of copolymer of LA and BnTMC **CP7**

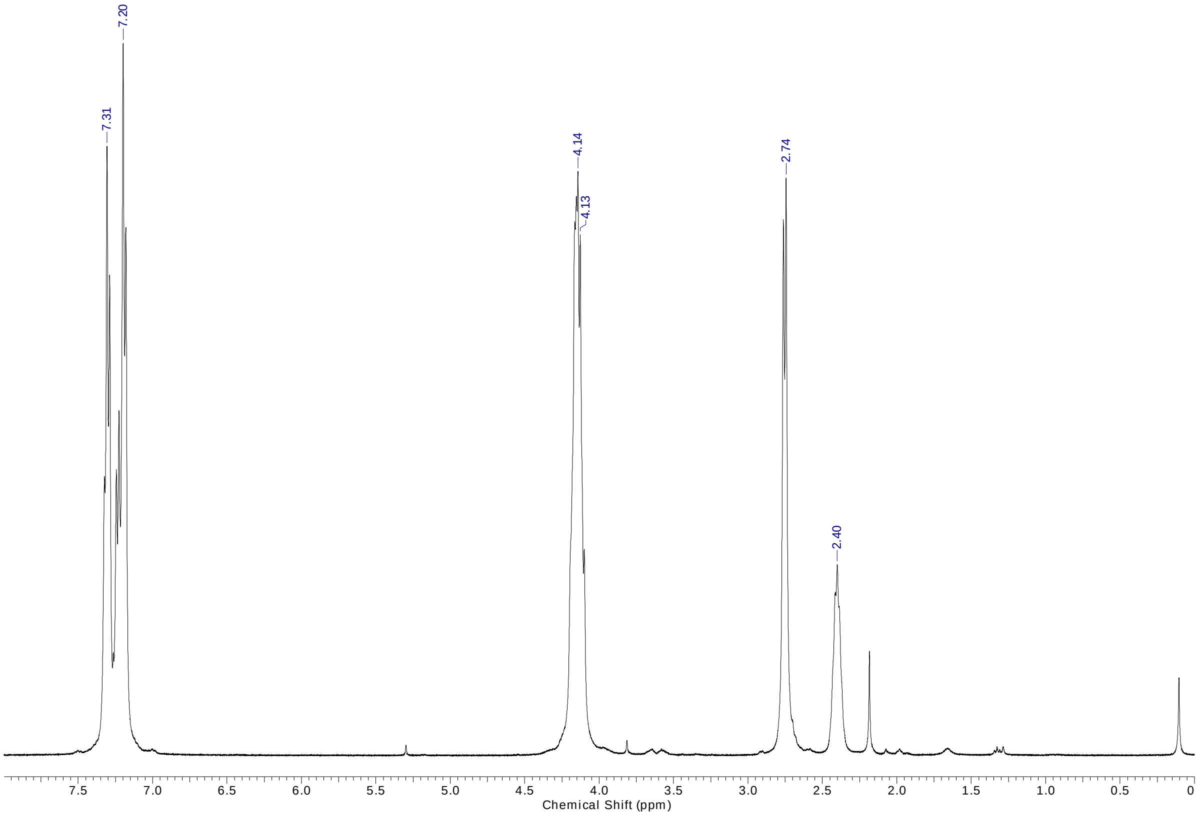


Figure S13.^{1}H NMR spectrum of polyBnTMC **P3**

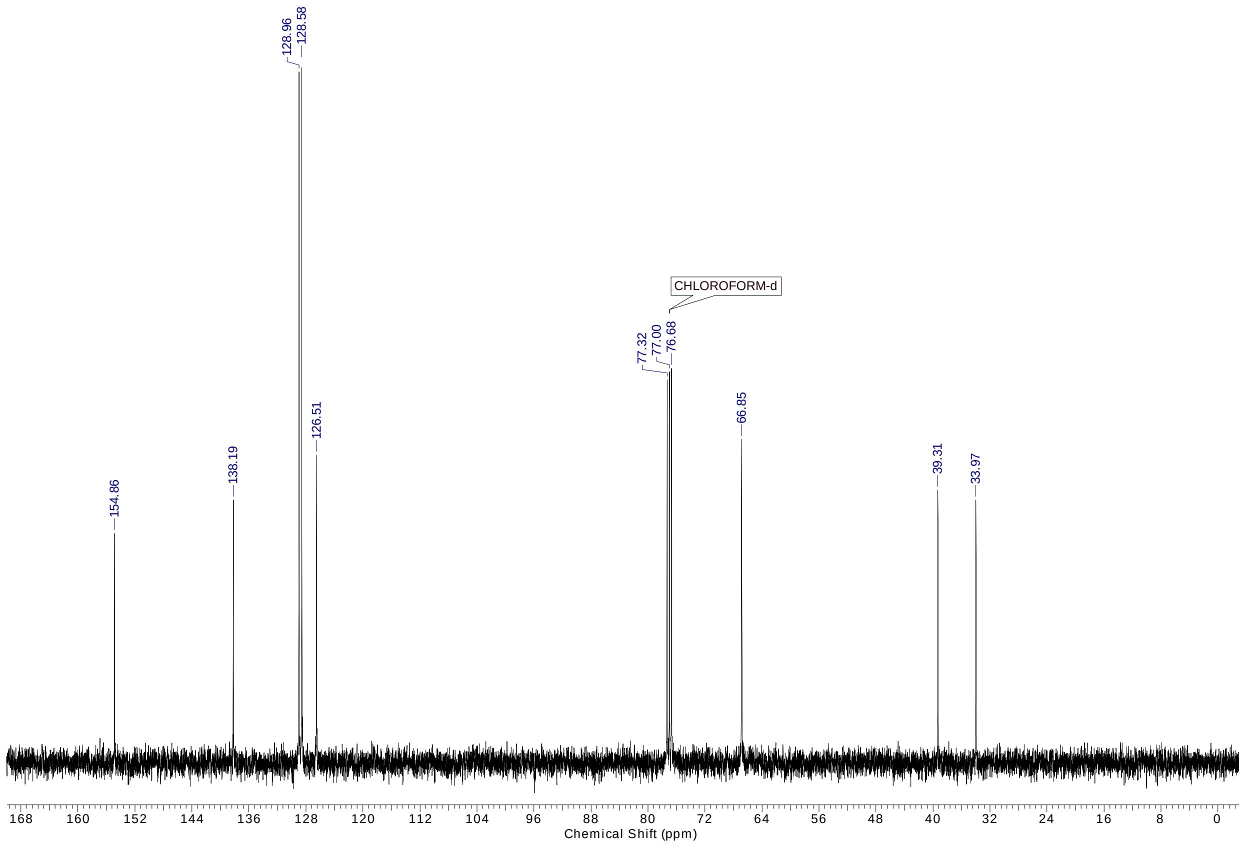


Figure S14. ^{13}C NMR spectrum of polyBnTMC **P3**

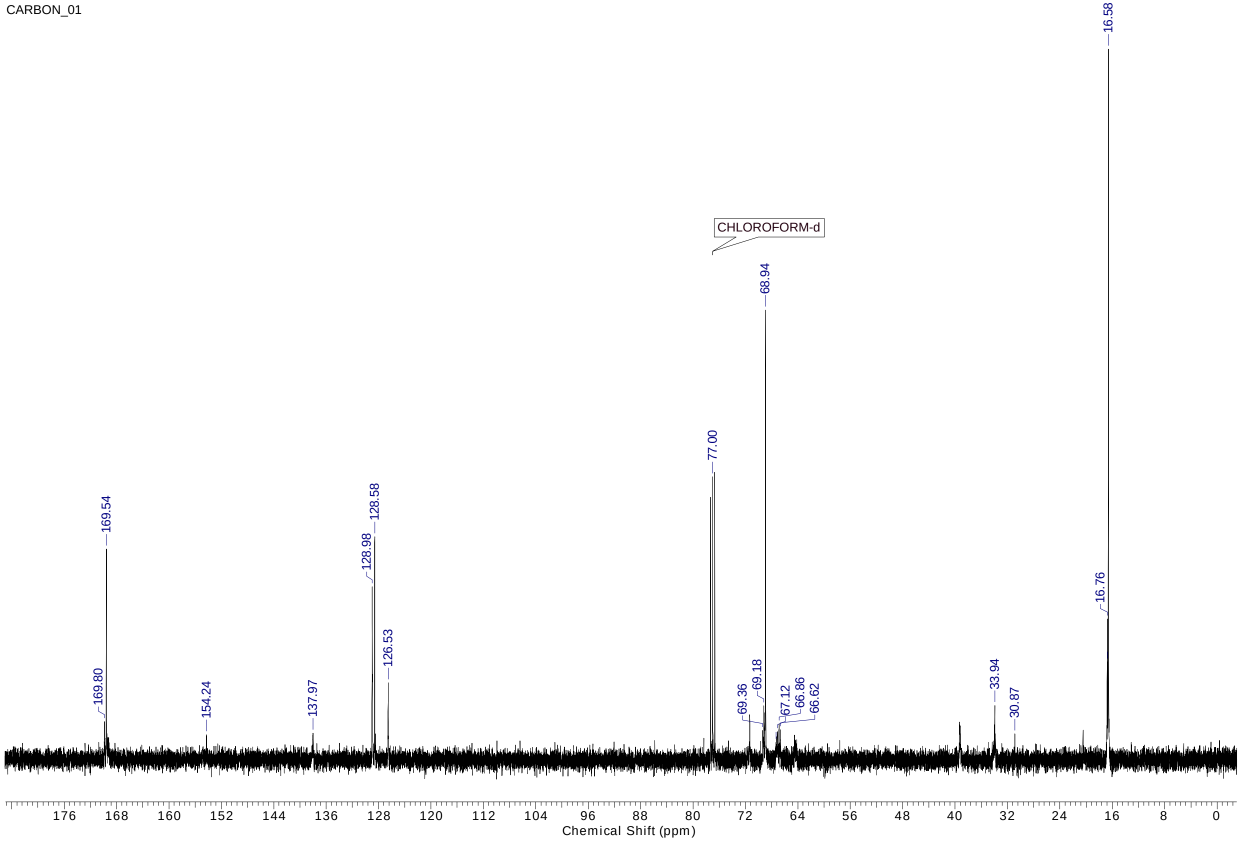


Figure S15. ^{13}C NMR spectrum of of copolymer of LA and BnTMC **CP7**

DOSY NMR spectrum of copolymer CP7

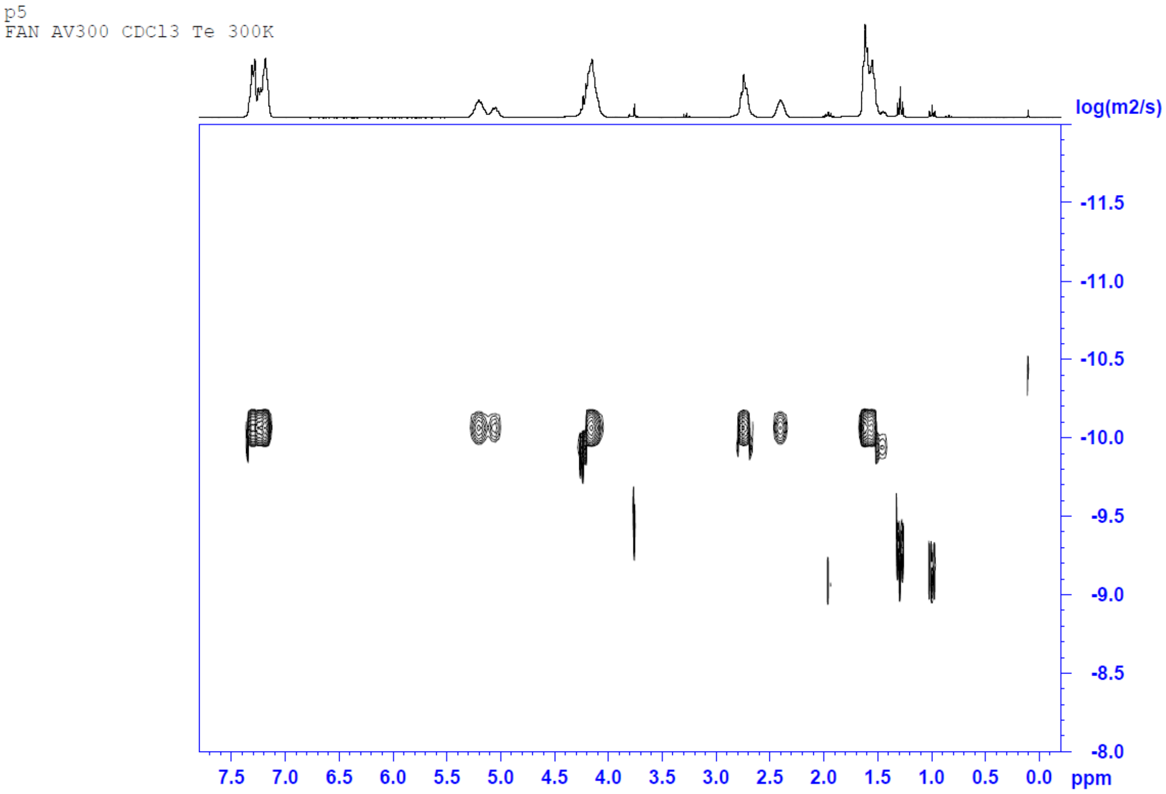


Figure S16. DOSY NMR spectrum of copolymer of BnTMC and LA **CP7**

Table S2. DOSY NMR Data.

Chemical shift value, ppm	$D \times 10^{-11}$ /m^2 s^{-1}	Compound
1.616	7.819	copolymer of BnTMC and L-LA
2.401	8.136	copolymer of BnTMC and L-LA
2.743	8.206	copolymer of BnTMC and L-LA
4.153	7.950	copolymer of BnTMC and L-LA
5.203	7.983	copolymer of BnTMC and L-LA
7.186	7.969	copolymer of BnTMC and L-LA

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S3. S. Mirilashvili, N. Chasid-Rubinstein and A. Albeck, *Eur. J. Org. Chem.*, 2008, **20**, 3461; https://doi.org/10.1002/ejoc.200800334.
S4. E. Brenna, F. Cannavale, M. Crotti, V. de Vitis, F. G. Gatti, G. Migliazza, F. Molinari, F. Parmeggiani, D. Romano and S. Santangelo, *ChemCatChem*, 2016, **8**, 3796; https://doi.org/10.1002/cctc.201601051.