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[Electronic Supplementary Information]

Synthesis of a Series of Biodegradable Poly(butylene carbonate-co-isophthalate) Random Copolymers Derived from CO2-based Comonomer for Sustainable Packaging

Kwang Hyun Paek,[a,b] and Sung Gap Im[*a]

[a] Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea

[b] Lotte Chemical Research Institute, 115 Gajeongbuk-ro, Yuseong-gu, Daejeon 34110, Korea

Correspondence to S. G. Im

e-mail: sgim@kaist.ac.kr

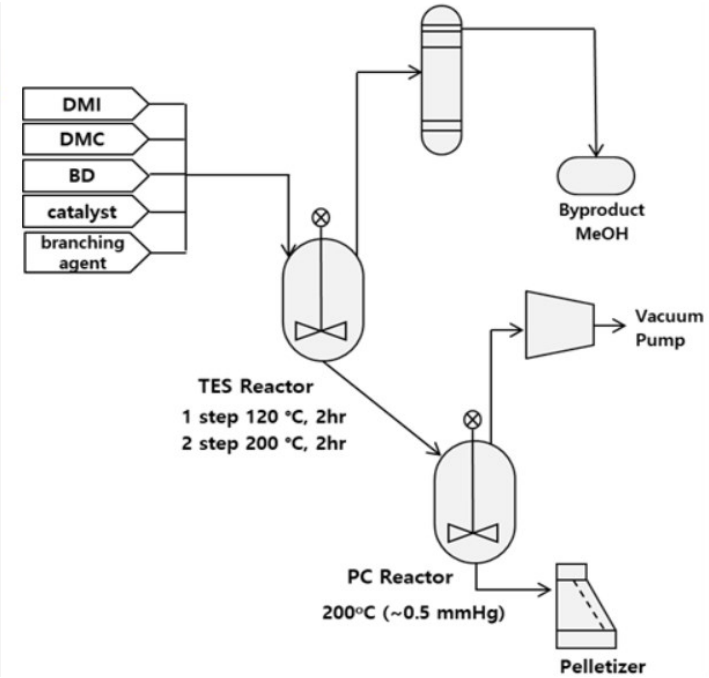
Fax: +82-42-350-3910

Table S1. Analysis of $PBCP_{50}$, $PBCI_{50}$ and $PBCT_{50}$.

Sample	[BC]/[BI] in feed	[BC]/[BI] in polymer	M_n (kg/mol)	M_w (kg/mol)	PDI	[η] (dL/g)
$PBCP_{50}$	50/50	47/53	6.3	18.3	2.88	0.32
$PBCI_{50}$	50/50	47/53	44	132	2.96	1.03
$PBCT_{50}$	50/50	49/51	47	133	2.78	1.05

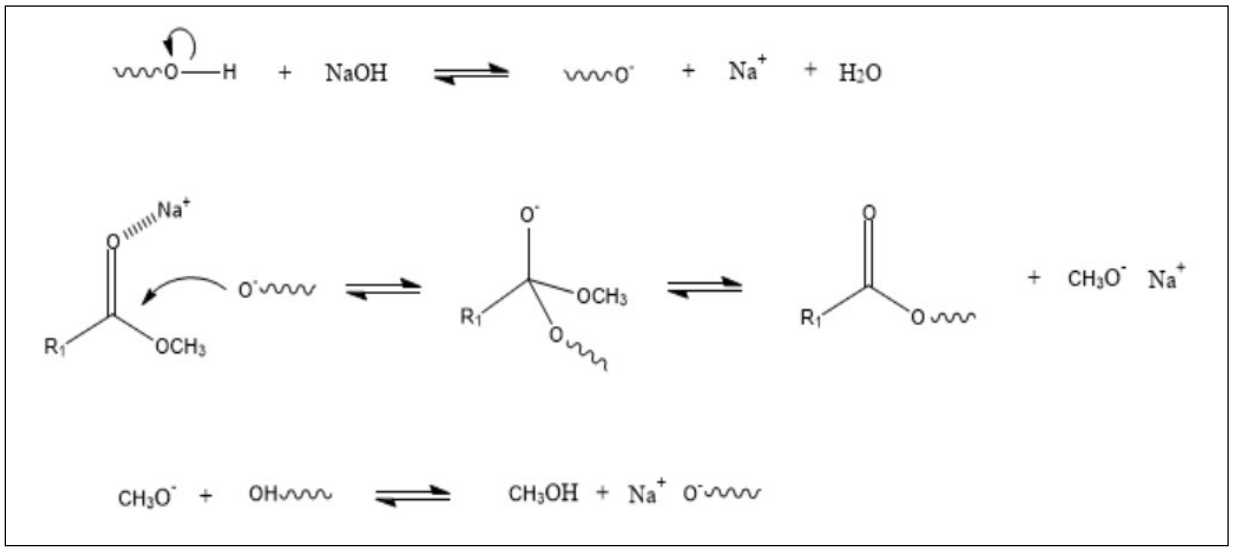
Poly(butylene carbonate-co-phthalate) (PBCP) copolymers were polymerized using DMP. The polymerization method was performed in the same manner as the **synthesis of PBCIs**. However, the copolymer with high molecular weight could not be synthesized and only the ones with low molecular weights (Mw lower than 20 kg/mol) were obtained due to the steric hindrance effect associated with the highly kinked structure of the DMP monomer [1]. In this study, our major focus was PBCIs whose property changes with the DMI content variation were assessed rigorously. In addition, PBCT copolymer was also polymerized using DMT in order to compare its physical properties with those of PBCIs (mechanical and optical properties and oxygen barrier, which are shown in **Table 4**).

Scheme S1. Schematic illustration of the bench-scale process.



Preparation of PBCIs Using a Bench Reactor. As shown in Scheme S1, a bench-scale system (12 L) was equipped with two reactors, mechanical stirrers and distillation column, and a vacuum system with liquid nitrogen cold trap and vacuum pump. In the first step of the transesterification (TES) reaction, BD, DMC, and DMI were used as comonomers. DMC and DMI were combined in a ratio determined by the content of BD. To polymerize PBCI 50, BD (2,500 g, 27.7 mol), DMC (2,498 g, 27.7 mol), DMI (2,693 g, 13.8 mol), NaOH (2.2 g, 0.20 mol % per BD) and glycerol propoxylate (9.2 g, 0.125 mol % per BD) were added to the TES reactor with N_2 purge. As the temperature increased, the mixed materials began to melt. Then the mixture was heated to 120 °C and stirred at 80 rpm for 2 hr. In the first step of the TES reaction, when the temperature at the top of the column falls below 60 °C (reduced TES reaction), the reaction temperature is increased from 120 °C to 200 °C for 0.5 hr and maintained for 1.5 hr while continuously distilling off the volatile byproducts from the transesterification reaction. The transesterification reaction proceeded to reach 95% of the theoretical amount of methanol was distilled out. The polycondensation was carry out at 200 °C under a reduced pressure of 200 mmHg for 0.2 hr, 100 mmHg for 0.2 hr, 50 mmHg for 0.3 hr, and 5 mmHg for 0.3 hr. Finally, polycondensation was conducted at 200-250 °C at 0.5 mmHg for 1.5 hr and the polymerization was stopped when a constant maximal torque value was measured. All melt polymers were cooled in a water bath and pelletized into small chips.

Scheme S2. Reaction mechanism of base-catalyzed transesterification reaction.



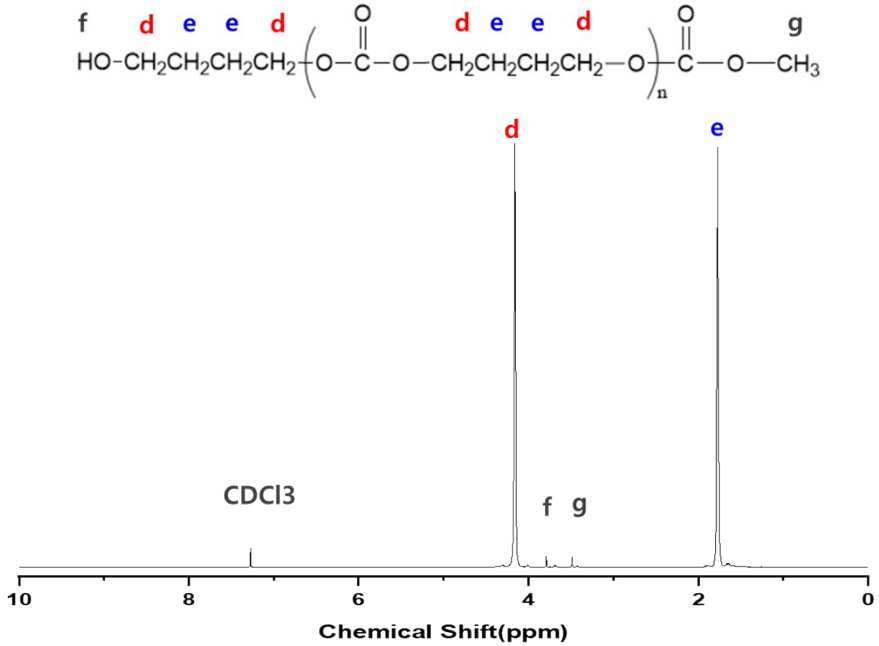


Figure S1. Analysis of PBC by ^{1}H-NMR.

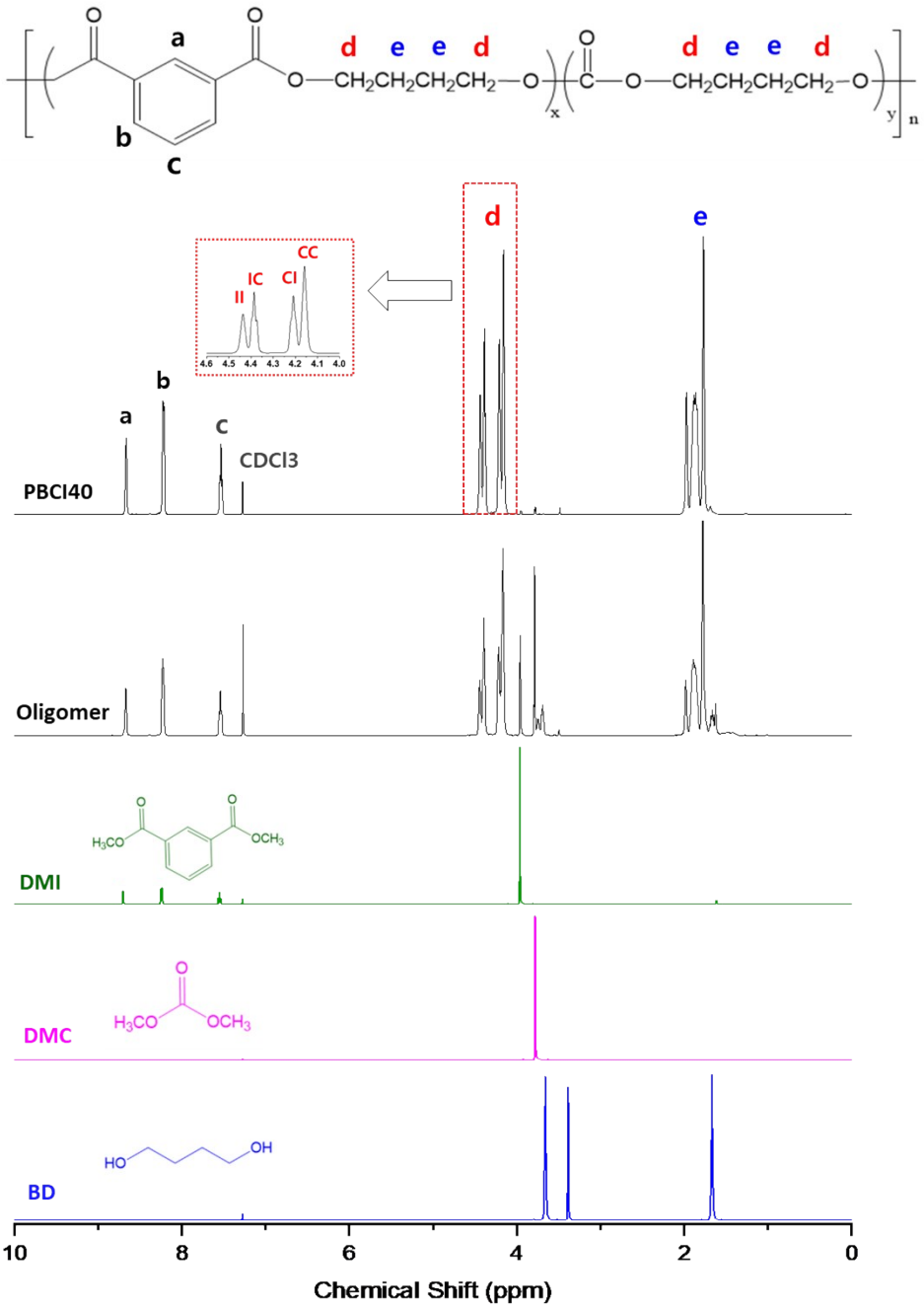


Figure S2. Analysis of PBCI40, oligomer and monomers by ^{1}H-NMR.

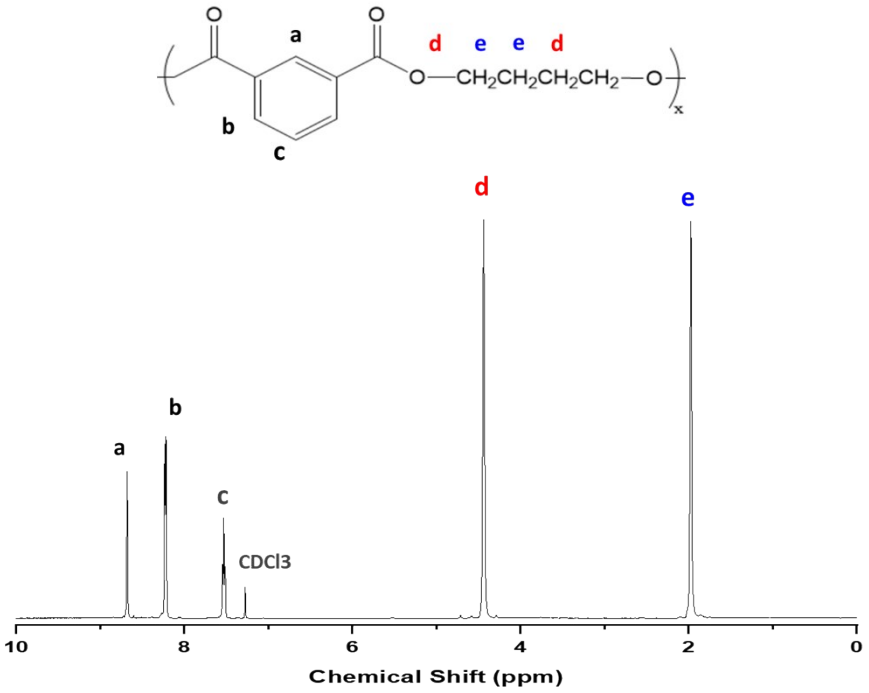


Figure S3. Analysis of PBI by ^{1}H-NMR.

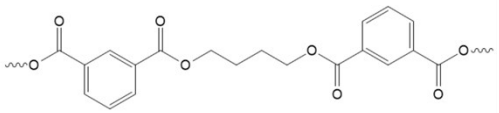
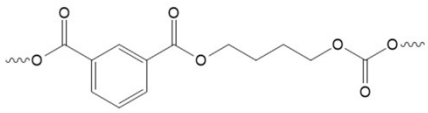
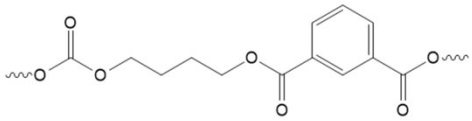
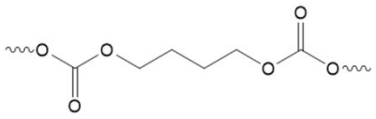
	Chemical shift (δ)	Structural unit
II	4.44 ppm	
IC	4.38 ppm	
CI	4.21 ppm	
CC	4.15 ppm	

Figure S4. ^{1}H-NMR spectroscopy analysis of dyad fractions in the copolymer.

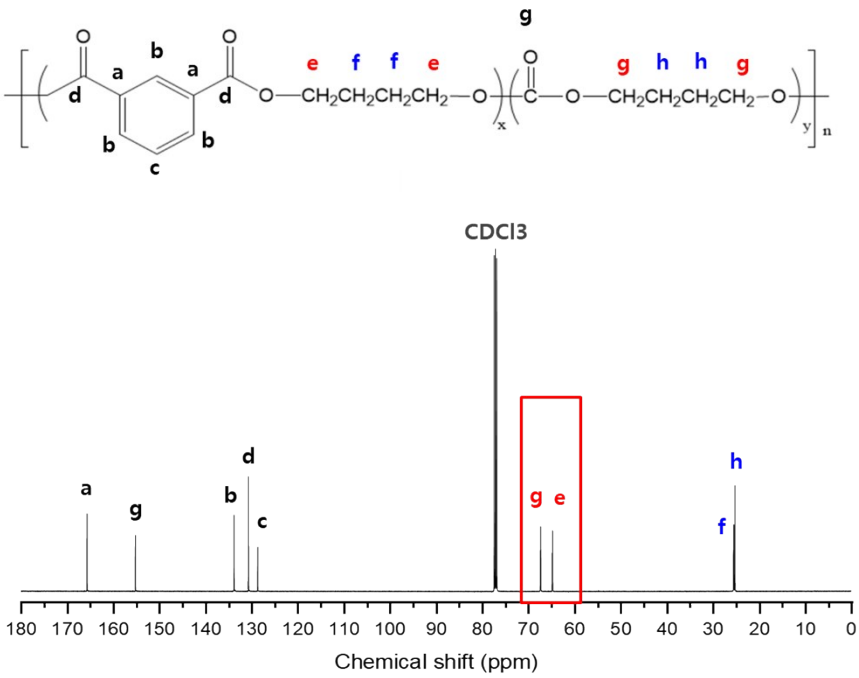


Figure S5. Analysis of PBCI40 by ^{13}C-NMR.

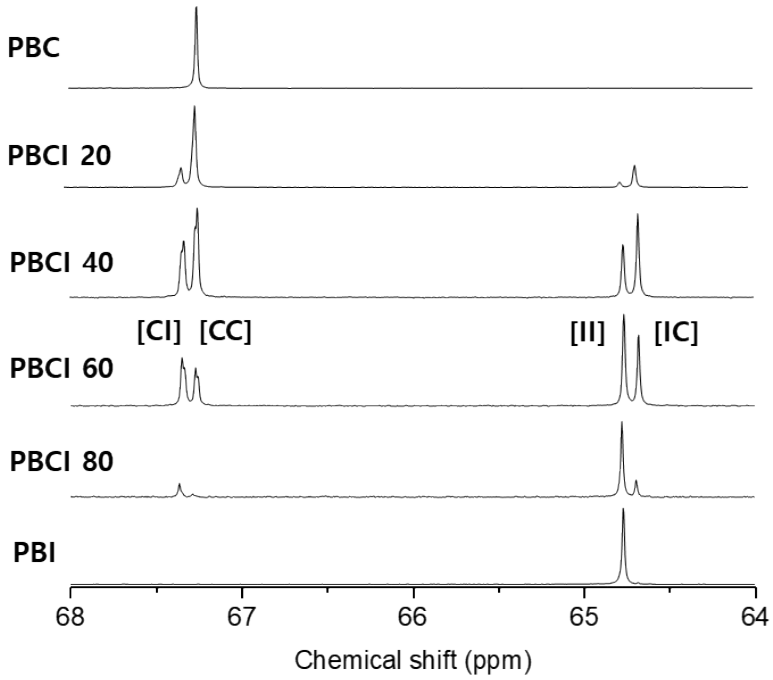


Figure S6. Analysis of PBC, PBCIs, PBI copolymers by ^{13}C-NMR.

Sample	[BC]/[BI] in polymer	$L_{n\,\mathrm{BC}}$	$L_{n\,\mathrm{BI}}$	R
PBC	100/0	-	-	-
PBCI 20	79.8/20.2	4.64	1.21	1.03
	80.2/19.8	4.61	1.20	1.01
PBCI 40	59.1/40.9	2.45	1.68	1.00
	59.6/40.4	2.47	1.68	1.00
PBCI 60	39.4/60.6	1.73	2.38	1.00
	42.1/57.9	1.72	2.35	1.00
PBCI 80	15.4/84.6	1.18	5.67	1.03
	17.4/82.6	1.19	6.14	1.00
PBI	100/0	-	-	-

Figure S7. Microstructure analysis of the PBCIs. (Black - ^{1}H NMR, Blue - ^{13}C NMR)

References

1 B. Lee, J. W. Lee, S. W. Lee, J. YooN and M. Ree, *Polymer Engineering & Science*, 2004, **44**, 1682-1691.