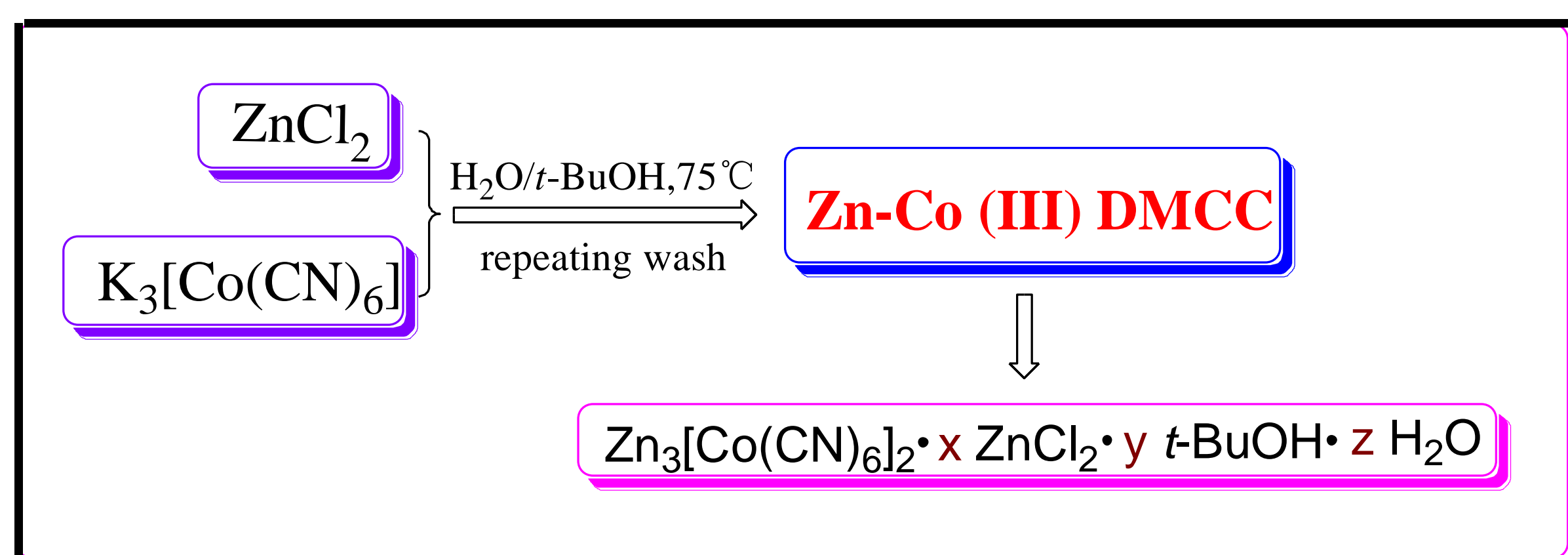


Introduction: As the growing concern on the carbon sequestration and storage process, the copolymerization of epoxide and CO₂ has attracted much attention. However, when the heterogeneous Zn-Co (III) double metal cyanide complex (Zn-Co (III) DMCC) is employed as catalyst, the resultant always shows relatively low carbonate ($F_{CO_2}\%$) and polymer selectivity ($W_{cc}\%$), with the production of ether linkage in the polymer and five-membered cyclic carbonate by-product. In order to overcome this problem, a nanolamellar Zn-Co (III) DMCC catalyst was prepared, and used for the styrene oxide(SO)/CO₂ copolymerization. It is found that the $F_{CO_2}\%$ was >99% and no cyclic carbonate was observed at low temperatures. Importantly, the SO/CO₂ reaction was confirmed to be regio-selective, resulting in head-to-tail (HT) content of 85-95%, which was determined by the $F_{CO_2}\%$. Other polar epoxides such as epichlorohydrin (ECH) and glycidyl methacrylate (GMA) were also carried out under the DMCC catalysis, resulted in functional poly(carbonate-co-ether) diols for post-modification.

1) Zn-Co (III) DMCC preparation



DMCC: simple, non-sensitive to air and water and robust.

2) The characterization of Zn-Co (III) DMCC

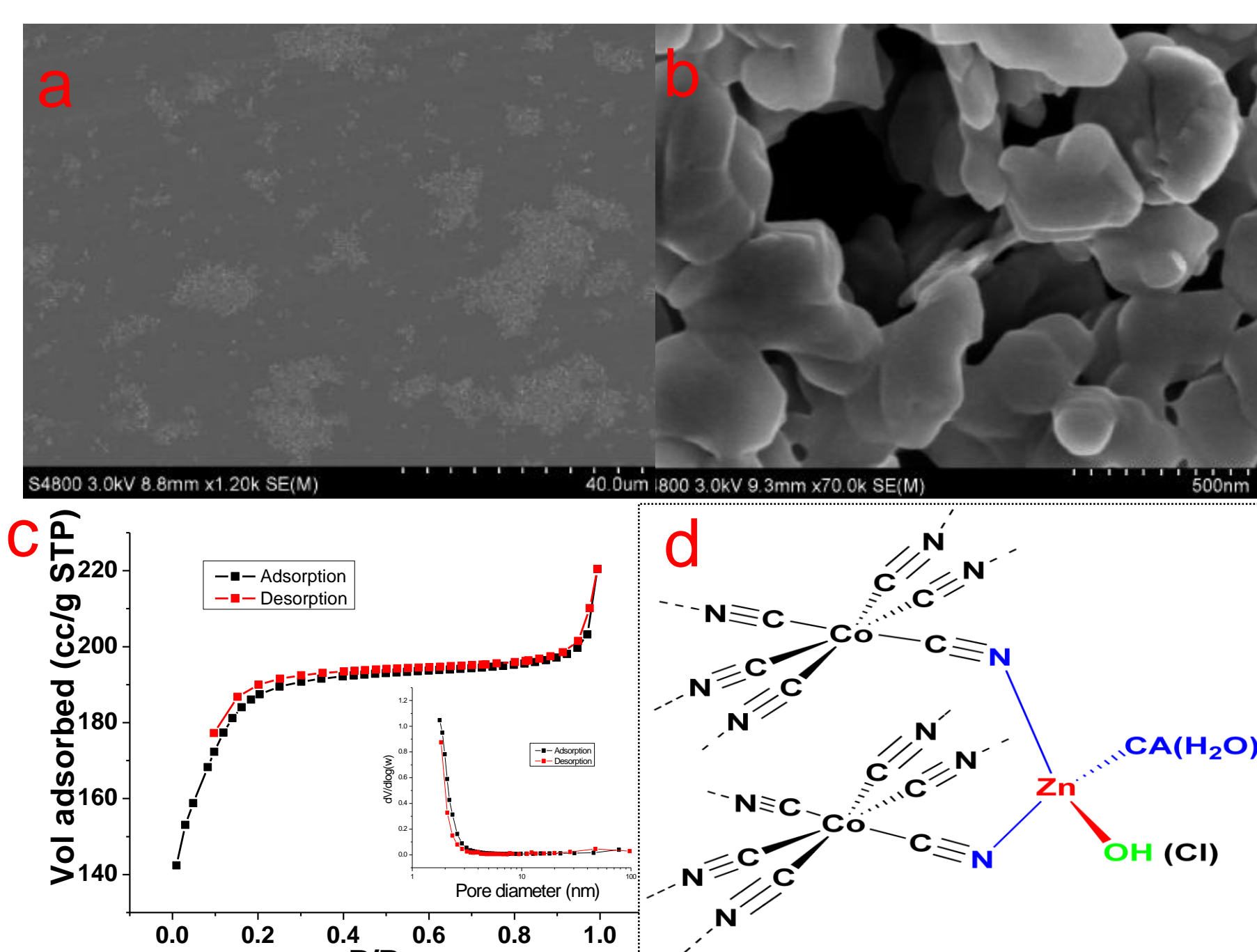
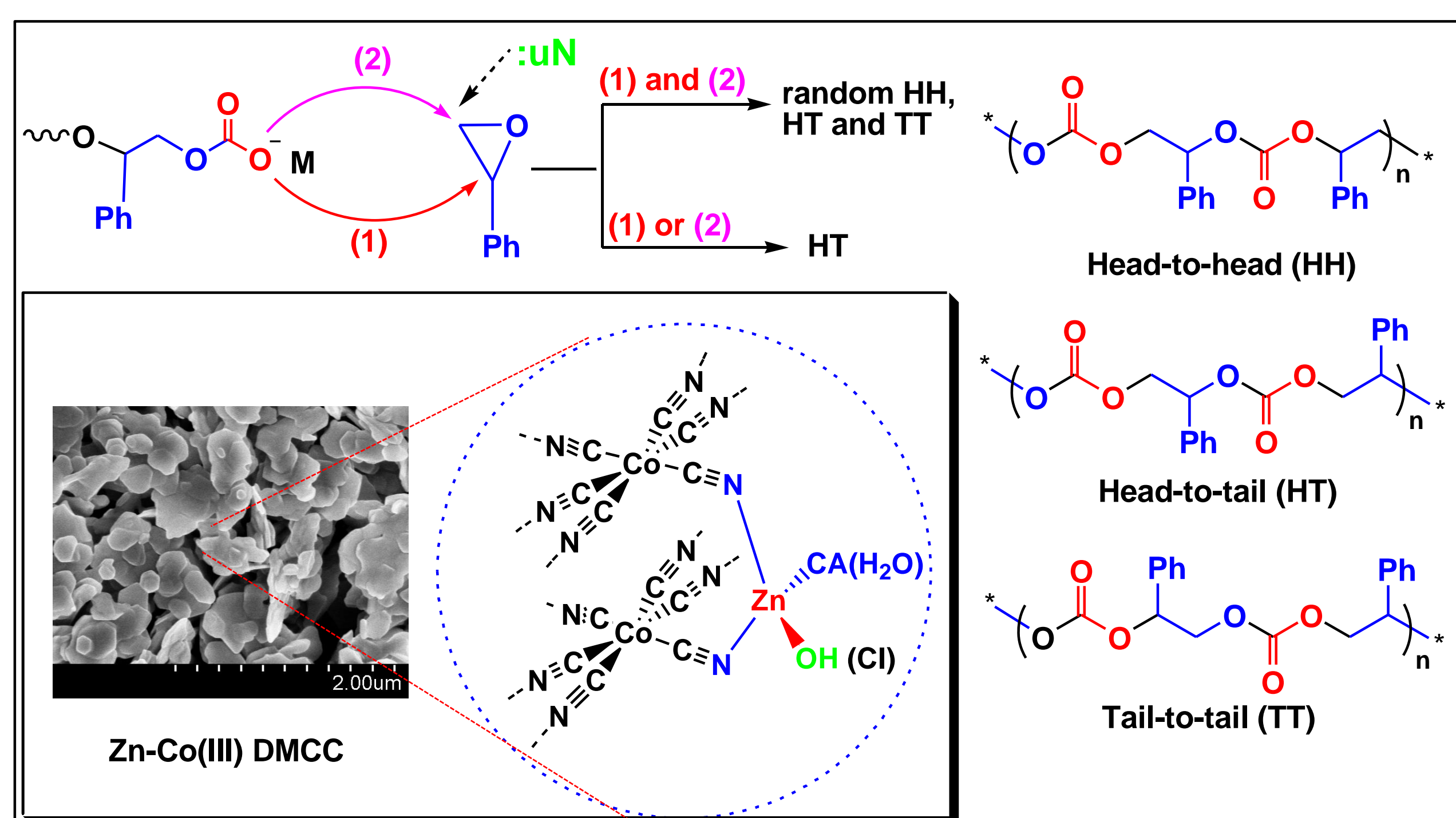
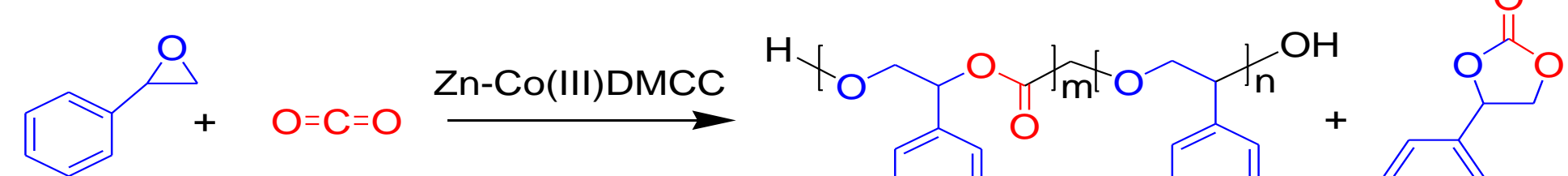


Figure 1. SEM images (a, b), N₂ absorption and desorption curve (c) and proposed Zn-OH initial structure (d) of Zn-Co(III) DMCC.

3) regio-selective ring-opening of SO



4) SO-CO₂ copolymerization catalyzed by Zn-Co (III) DMCC



Entry	Temp (°C)	Pressure (MPa)	$F_{CO_2}\%$ ^a	H-T content ^c	$W_{sc}\%$ ^b (wt%)	M_n (kg/mol)	PDI	T_g (°C)
1	90	4.0	44.1	-	60.3	3.5	2.8	15.9
2	60	4.0	91.1	85.3%	4.4	5.8	3.2	42.8
3	50	4.0	93.2	87.5	3.2	11.7	3.0	55.4
4	40	4.0	96.1	91.4%	1.4	25.0	2.3	81.2
5	35	4.0	97.8	94.4%	1.3	26.4	2.2	81.6
6	30	4.0	ND	ND	ND	ND	ND	ND
7	35	5.0	98.2	94.5%	1.1	25.8	2.6	82.0
8	35	3.0	97.2	93.6%	1.2	22.4	2.4	78.8
9	35	2.0	97.0	93.1%	1.2	19.8	2.4	69.8
11 ^c	35	4.0	99.2	95.7%	0	4.4	3.0	54.5
12 ^d	35	4.0	99.0	95.4%	0	4.8	3.0	54.2

Reaction condition: 3.0mg DMCC, 3.0mL SO, 10h. ^a: the carbonate selectivity in the resultant polymer; ^b: the cyclic carbonate content in the crude product; ^c: 2.0mL CH₂Cl₂ was added; ^d: 2.0mL THF was added.

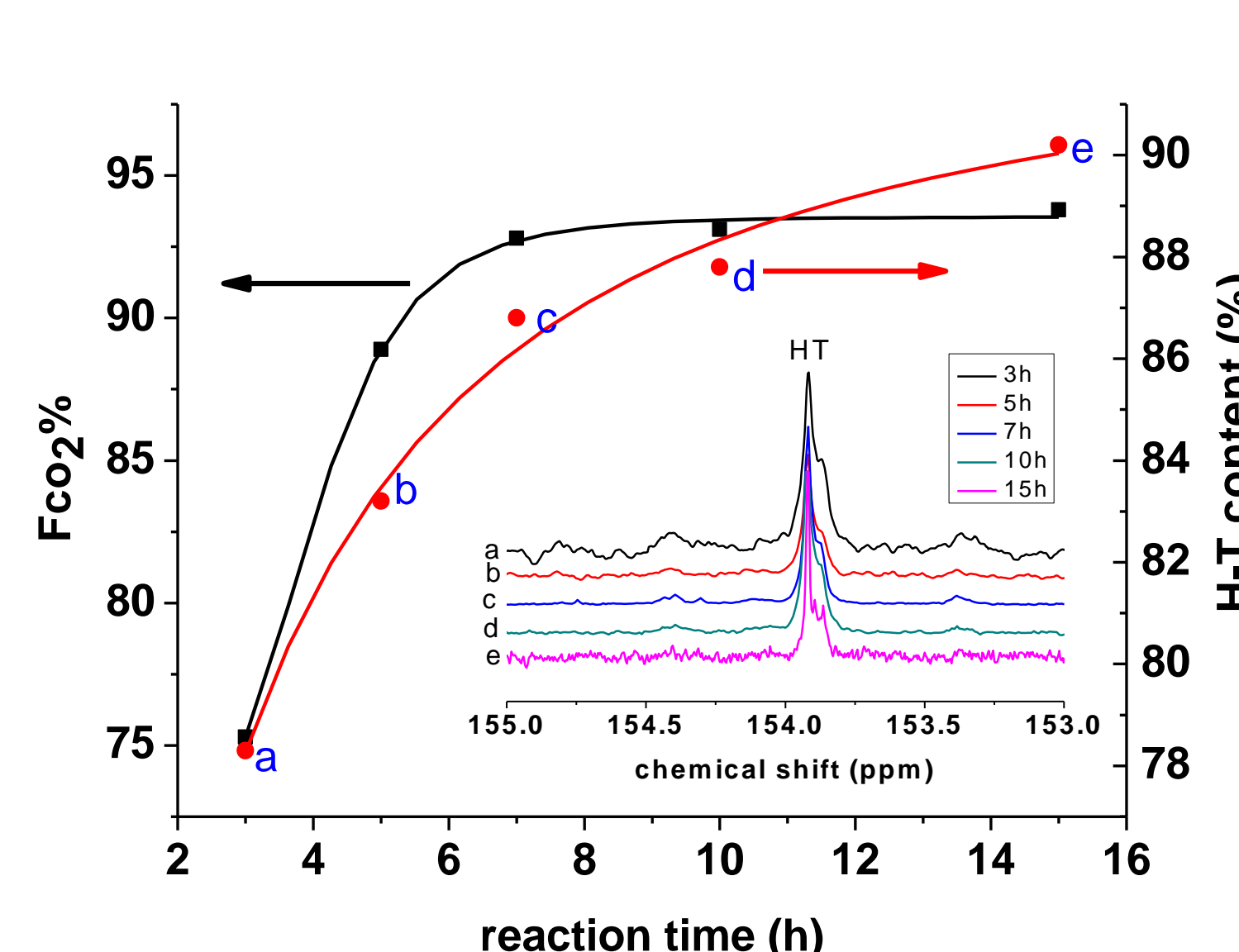


Figure 2. $F_{CO_2}\%$ and HT content vs reaction time.

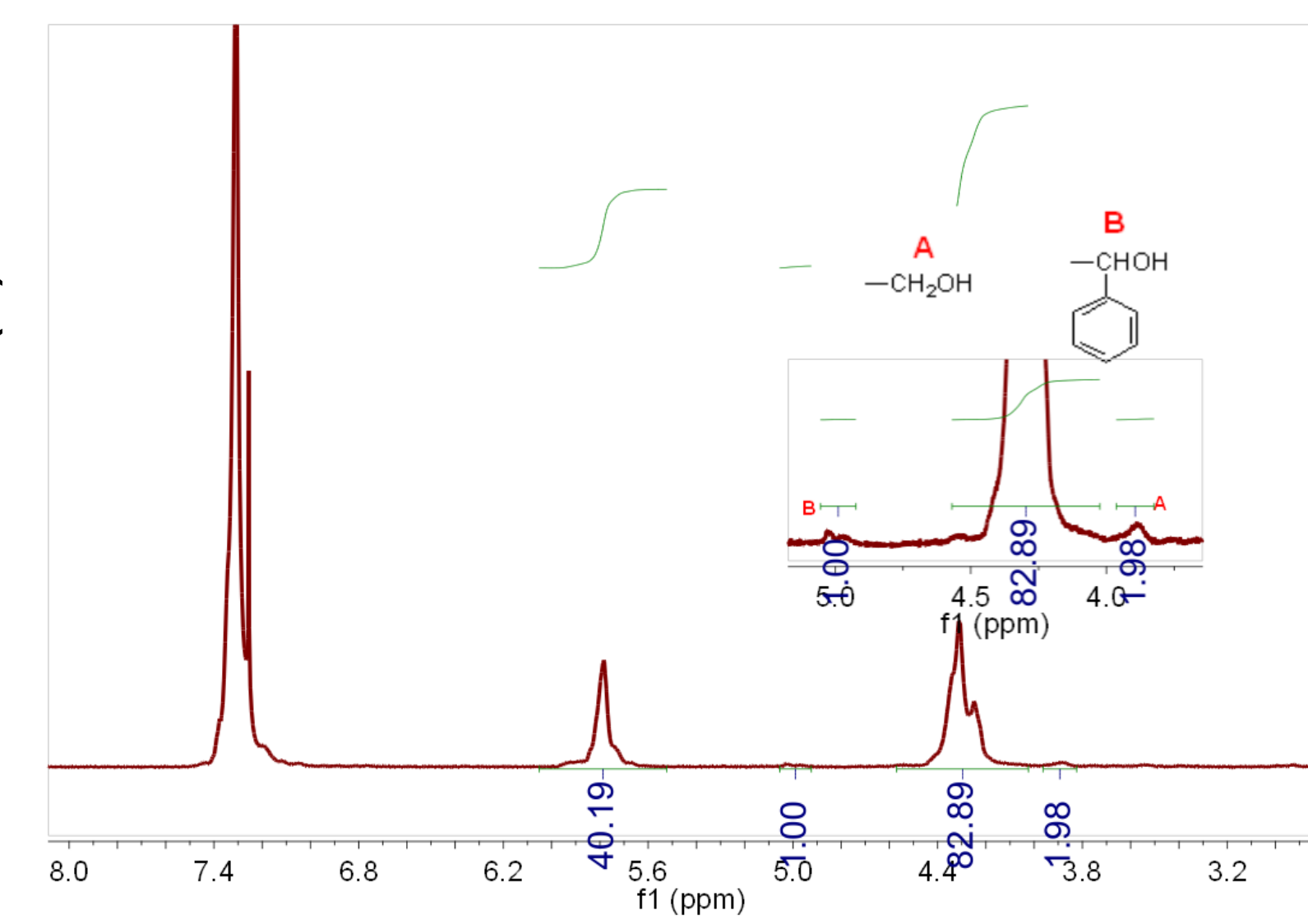


Figure 3. ¹H NMR spectrum of a SO-CO₂ copolymer with a $F_{CO_2}\%$ of 99.0%.

- 1) The SO-CO₂ copolymer catalyzed by DMCC showed a regio-selective microstructure, the head-to-tail (HT) content was up to 95.7%, which was determined by the $F_{CO_2}\%$ (Figure 2).
- 2) The SO-CO₂ copolymerization was initiated by Zn-OH structure, which produced terminal hydroxyl groups of -CH₂OH and -CH(Ph)-OH. The protons area was 2/1, as shown in Figure 3.

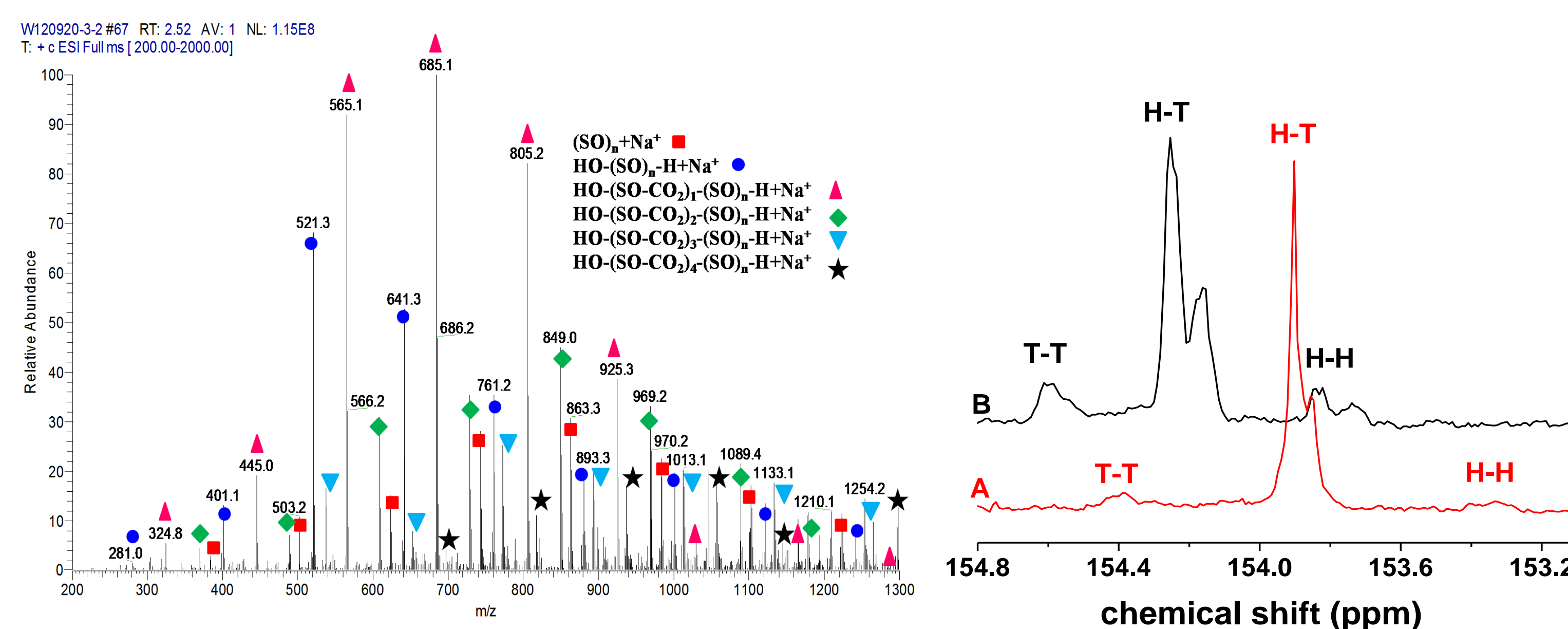
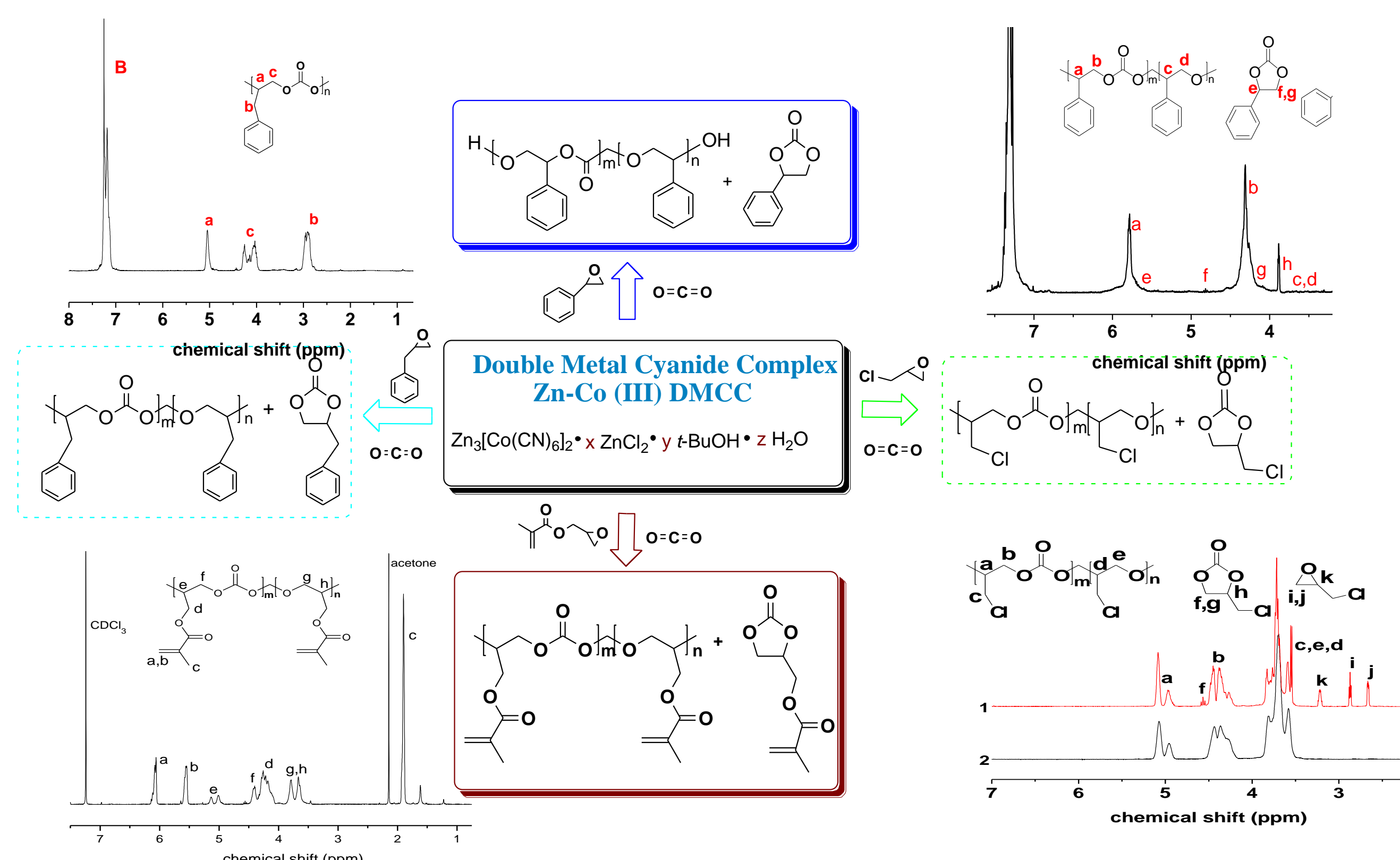


Figure 4. ESI-MS spectrum of SO-CO₂ copolymer catalyzed by DMCC catalyst.

Figure 5. ¹³C NMR spectra of SO-CO₂ (A) and 2-benzyloxirane-CO₂ (B) copolymers catalyzed by DMCC.

- 3) The resultant SO-CO₂ copolymer exhibited two terminal hydroxyl groups (Figure 4).
- 4) The electron-withdrawing ability of phenyl of SO was responsible for the regio-selective copolymerization with CO₂, while 2-benzyloxirane containing less electron-withdrawing ability displayed lower HT content (Figure 5).

5) Other polar epoxides copolymerization with CO₂ catalyzed by Zn-Co (III) DMCC



Acknowledgements

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