

# Ethylene/Propylene Copolymerization with Non-bridged Metallocene Catalyst: Reaction Kinetics and Thermal Properties



Yintian Guo, Zhisheng Fu, Zhiqiang Fan\*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization,

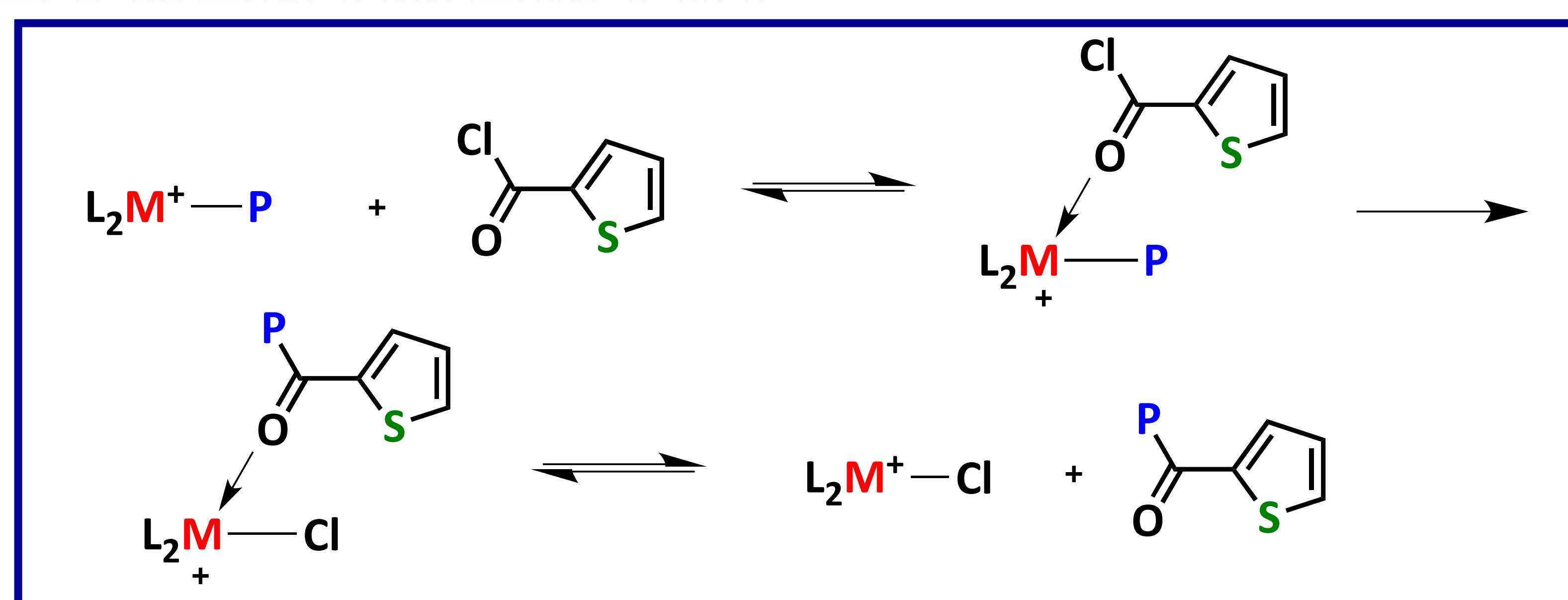
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China



## INTRODUCTION

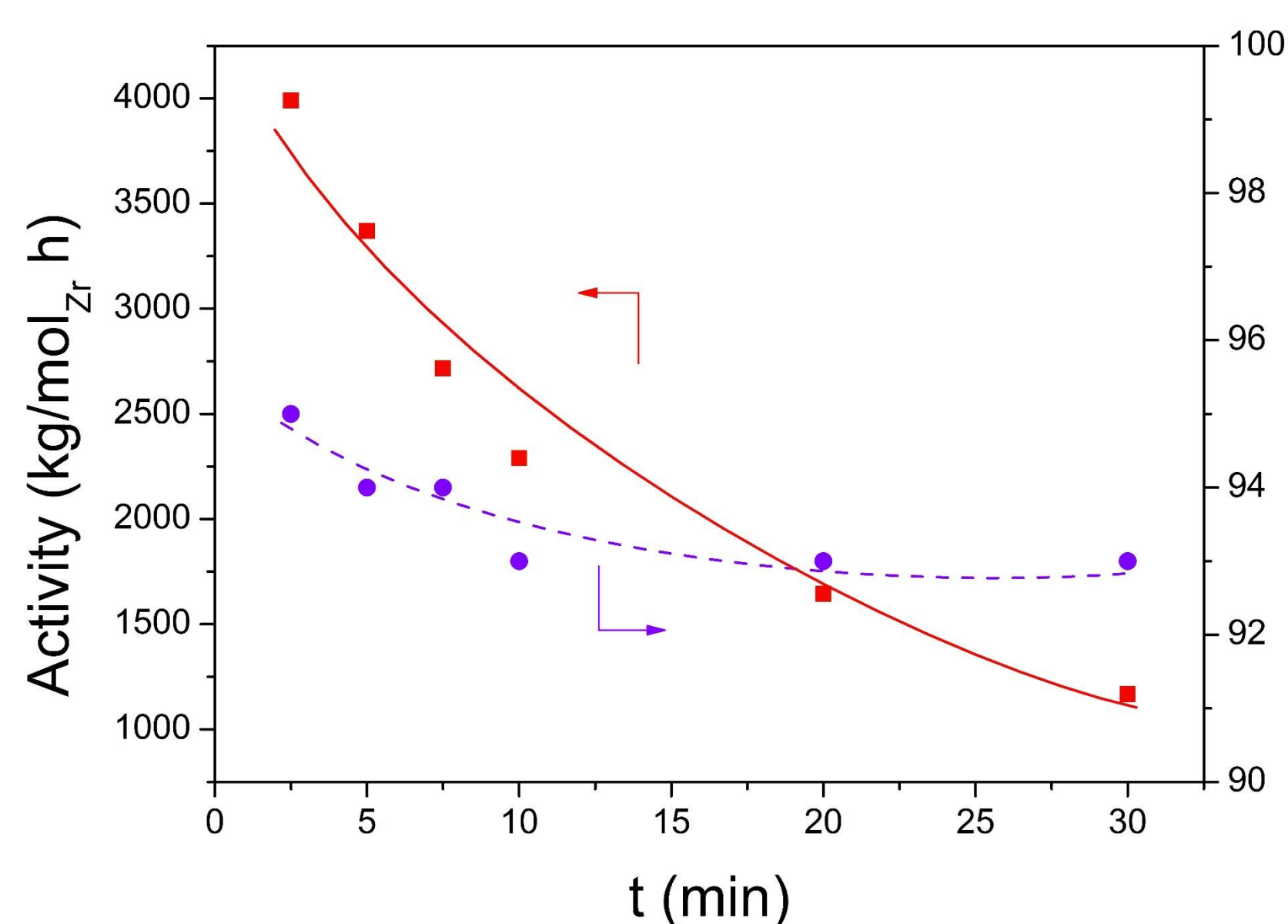
A series of ethylene/propylene copolymerization followed by quenching are successively conducted using non-bridged metallocene bis(2,4,7-trimethylindenyl)zirconium dichloride at atmospheric pressure and high temperature. Kinetic and thermal study are carried out to investigate changes in number of active centers, propagation rate constants, and polymer structure during the polymerization. All copolymers are found with broad molecular weight distribution, high melting temperatures, medium melting enthalpies and low glass transition temperatures. Further NMR and SSA tests prove the propylene units are isolated in the copolymer chain.

## EXPERIMENTAL

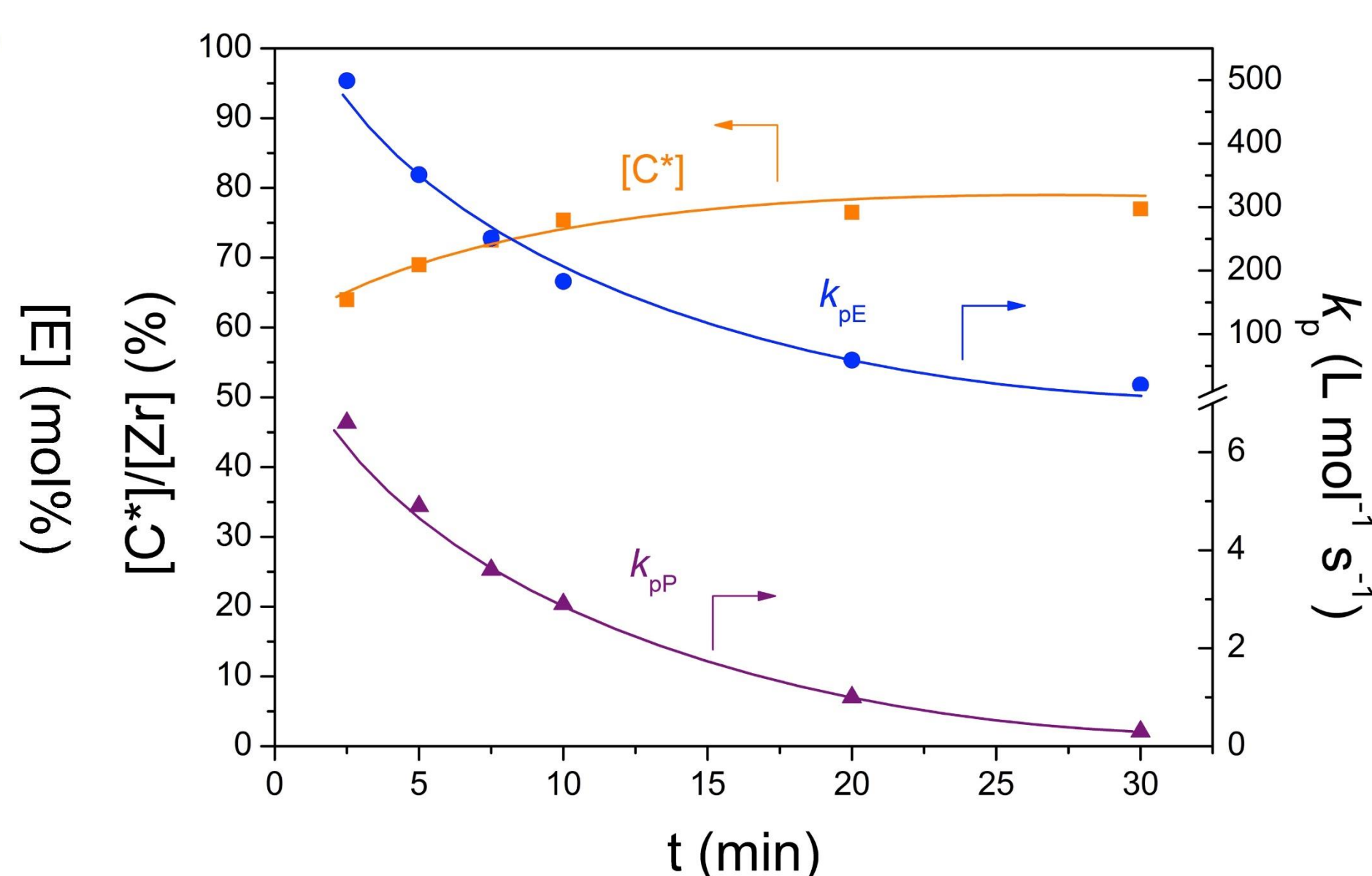


**Scheme 1.** Quenching reactions with 2-thiophenecarbonyl chloride. Reaction conditions: 1.25  $\mu$ mol bis(2,4,7-trimethylindenyl)zirconium dichloride, 50  $^{\circ}\text{C}$ , MAO/Zr = 1000, 50 mL toluene, 2-thiophenecarbonyl chloride/Al = 2, quenching time = 5 min, 1 atm,  $P_{\text{ethylene}} : P_{\text{propylene}} = 0.66 : 0.34$ .

## DISCUSSION

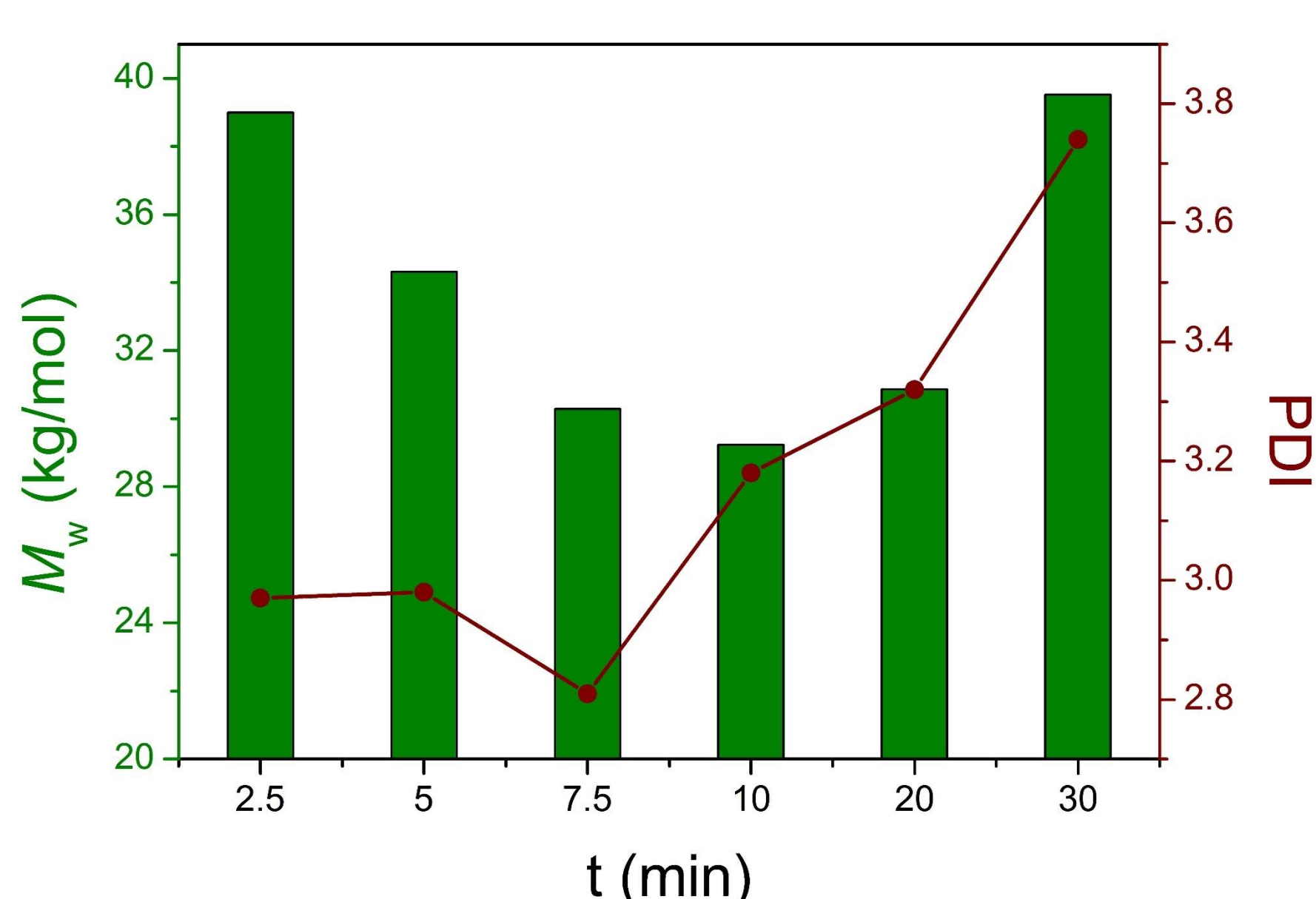


**Fig 1.** Influences of time on activity and content of ethylene.

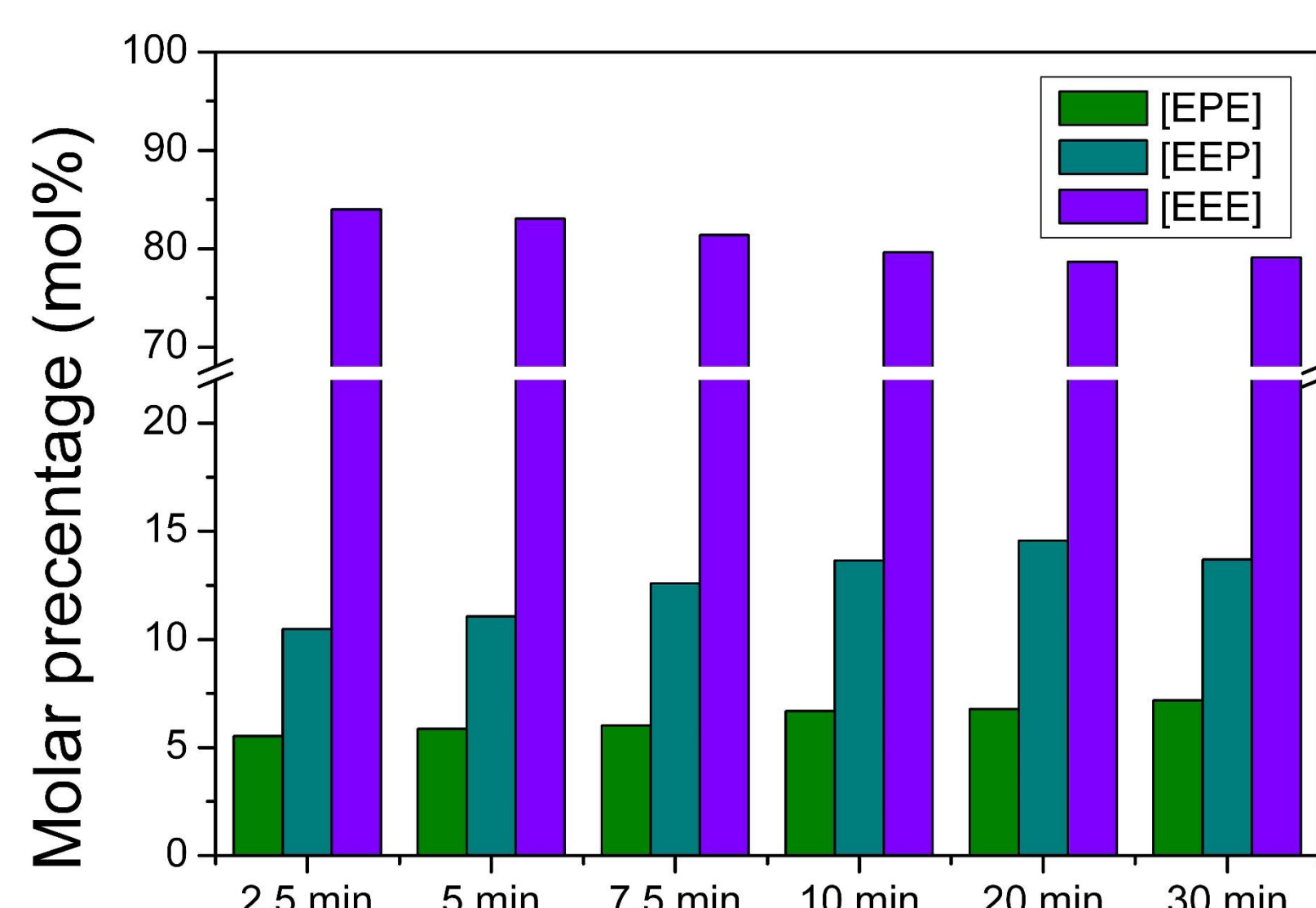


**Fig 2.** Influences of time on number of active centers and propagation rate constants ( $k_p$ ).

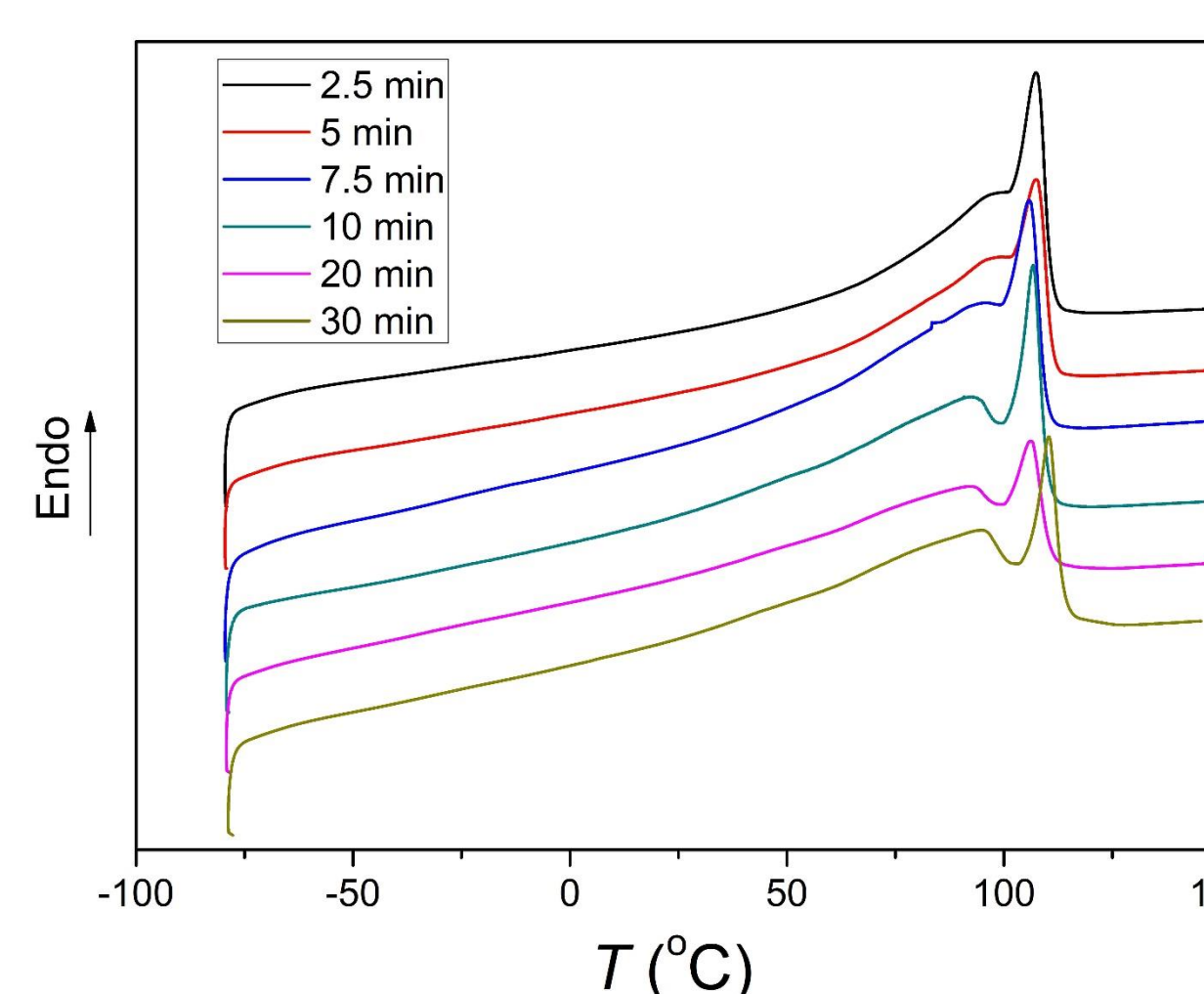
High concentration of active centers was achieved from the very beginning. Similarly rapid decline in both  $k_{pE}$  and  $k_{pP}$  values with time were observed. A broad molecular weight distribution was observed for each copolymer, indicating existence of multiple active centers. Also, Only [EEE], [EEP] and [EPE] triads were observed, indicating the insertion pattern of propylene was mostly in a isolated manner.



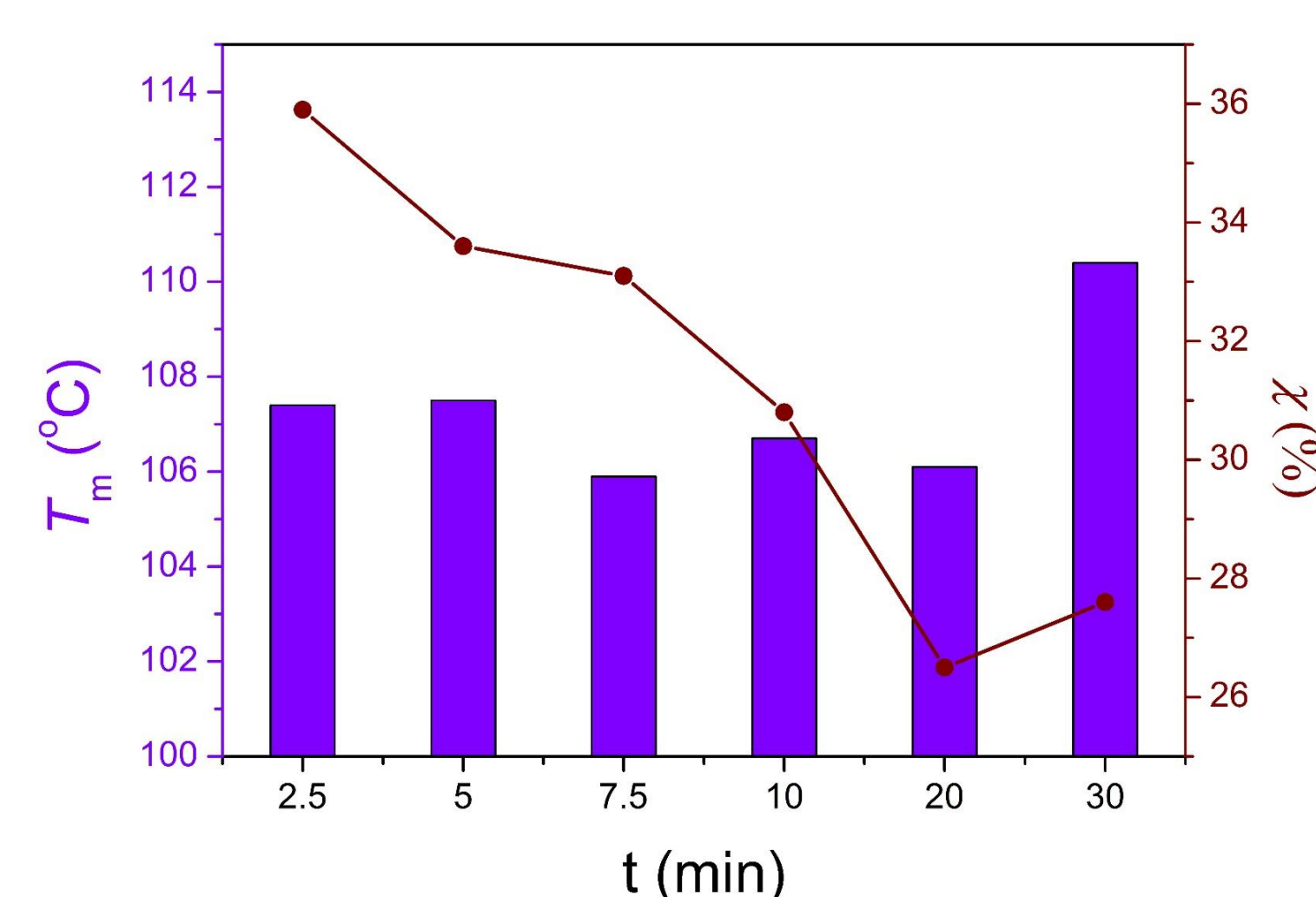
**Fig 3.** Weight-average molecular weight and PDI for copolymers at different time.



**Fig 4.** The contents of [EEE], [EPE] and [EEP] triads at different time.

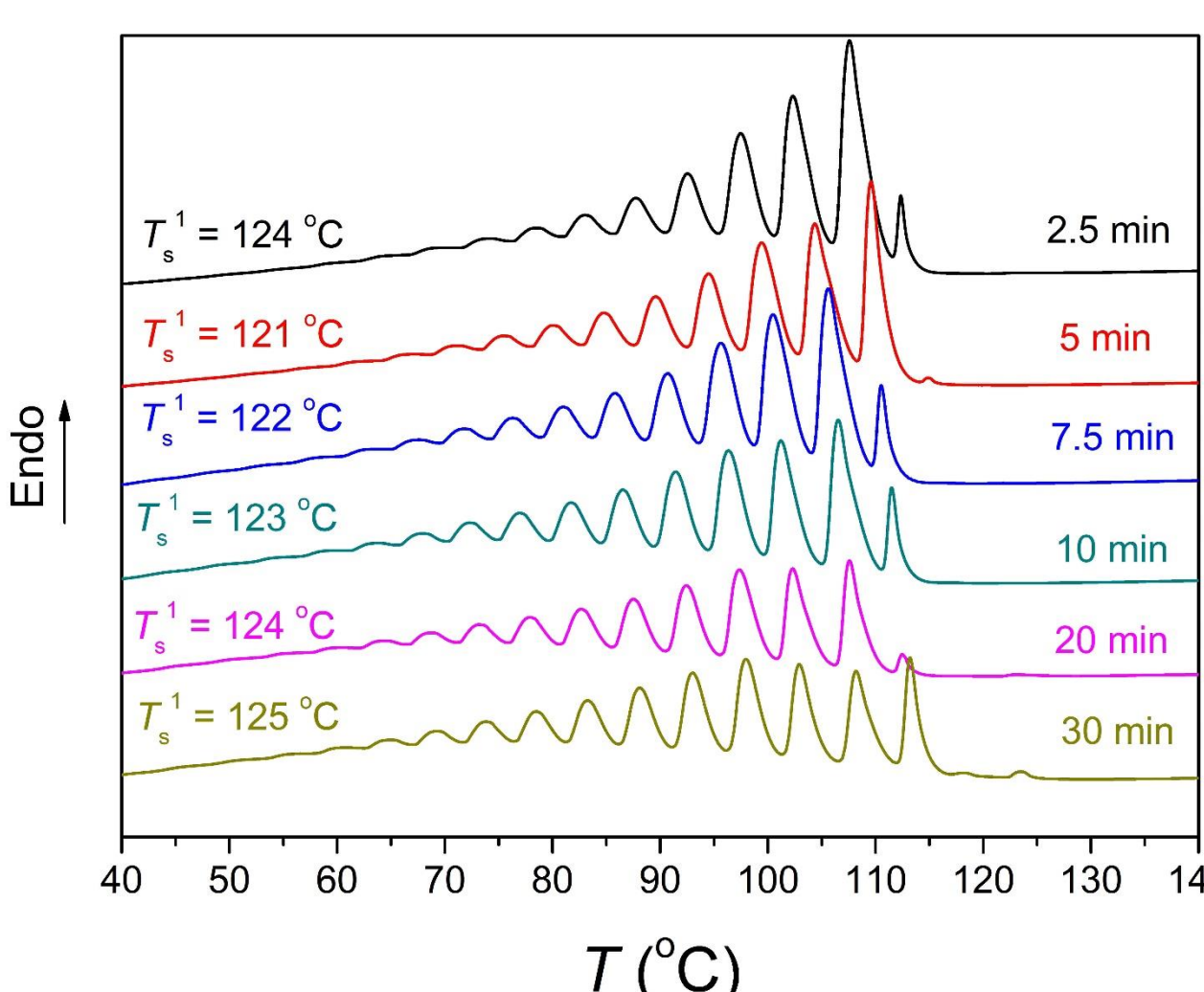


**Fig 5.** DSC melting curves of copolymers.

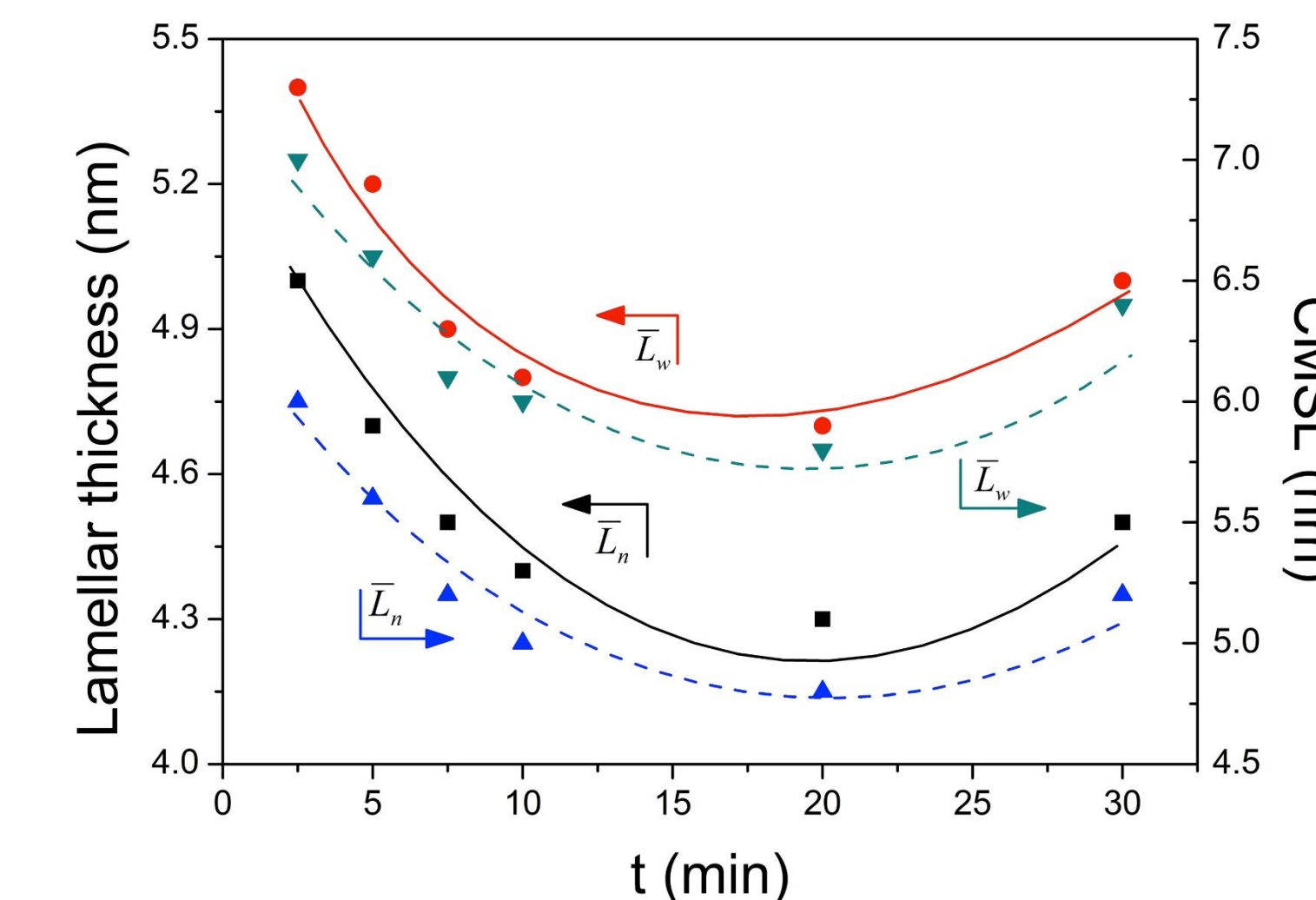


**Fig 6.** Melting temperatures and crystalline degree of copolymers.

Broad melting range or even bimodal melting peaks were detected for copolymers, and SSA treatments were then adopted to analyze details of chain structure. Multi-peaks ranging from 40 to 125  $^{\circ}\text{C}$  were observed for all copolymers after SSA treatment. Thinner lamellae and shorter crystalline methylene sequence were generated with time, indicating the frequency of propylene units insertion increased with time.



**Fig 6.** Melting traces of copolymers after SSA treatment.



**Fig 7.** Number- and weight-average of lamellar crystal thickness and CMSL of copolymers.

## CONCLUSIONS

More than 60 % of catalyst precursors are found activated as active centers at initial stage, indicating a rapid activating period.  $k_p$  values of ethylene are about 70 times faster than those of propylene at any set point. A broad molecular weight distribution is observed for each copolymer, which is resulted from multiple types of active centers.

Multiple melting peaks are observed after SSA treatment for all copolymers. Contents of thinner lamellar crystals increases with time, indicating more propylene was inserted in the later stage.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] X. R. Shen, J. Hu, Z. S. Fu, J. Q. Lou, Z. Q. Fan, *Catal. Commun.* **2013**, 30, 66.
- [2] Z. Z. Tong, Y. Huang, J. T. Xu, Z. S. Fu, Z. Q. Fan, *J. Phys. Chem. B* **2015**, 119, 6050.