

Introduction

- Non-catalytic hydrothermal dechlorination is conventionally described as a single-stage process due to methodological inconsistencies
- While the mechanism is dynamic with respect to dechlorination degree, kinetics are treated as constant
- This work presents a more comprehensive kinetic analysis which shows the dynamic nature of hydrothermal kinetics
- Reaction kinetics are also dependent on the degree of polymerization of the PVC polymer

Objectives

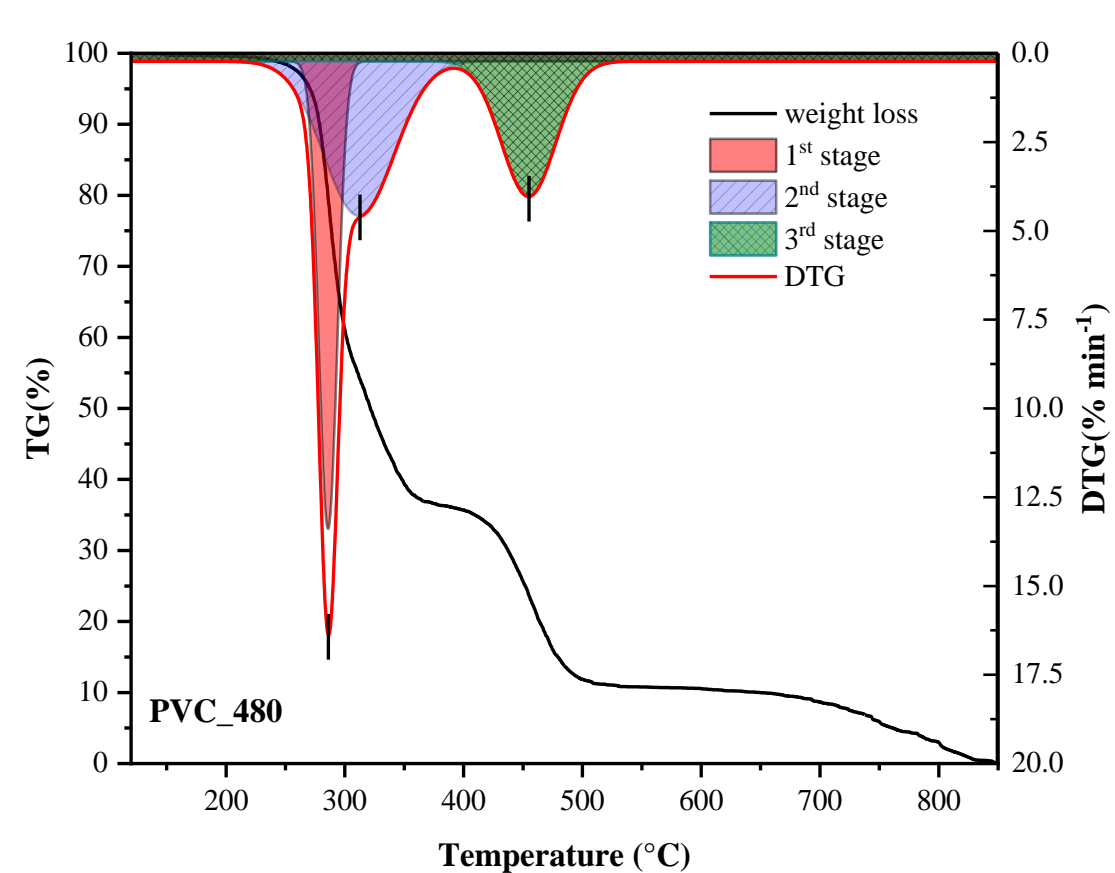
- To determine hydrothermal dechlorination kinetics for different PVCs
- To study the effect of polymerization degree on dechlorination behavior
- Evaluate changes in mechanism with respect to dechlorination degree

Material and Methods

- PVCs of polymerization degree (DP) 480, 1050, and 3000 were used
- Hydrothermal conditions - PVC/Water ratio of 1: 100
 - Temperature 200 - 250°C
 - Time 1 - 9hrs
- Characterization: Thermogravimetric analysis, Ion chromatography, XPS FTIR, and Elemental Analysis

Results and Discussion

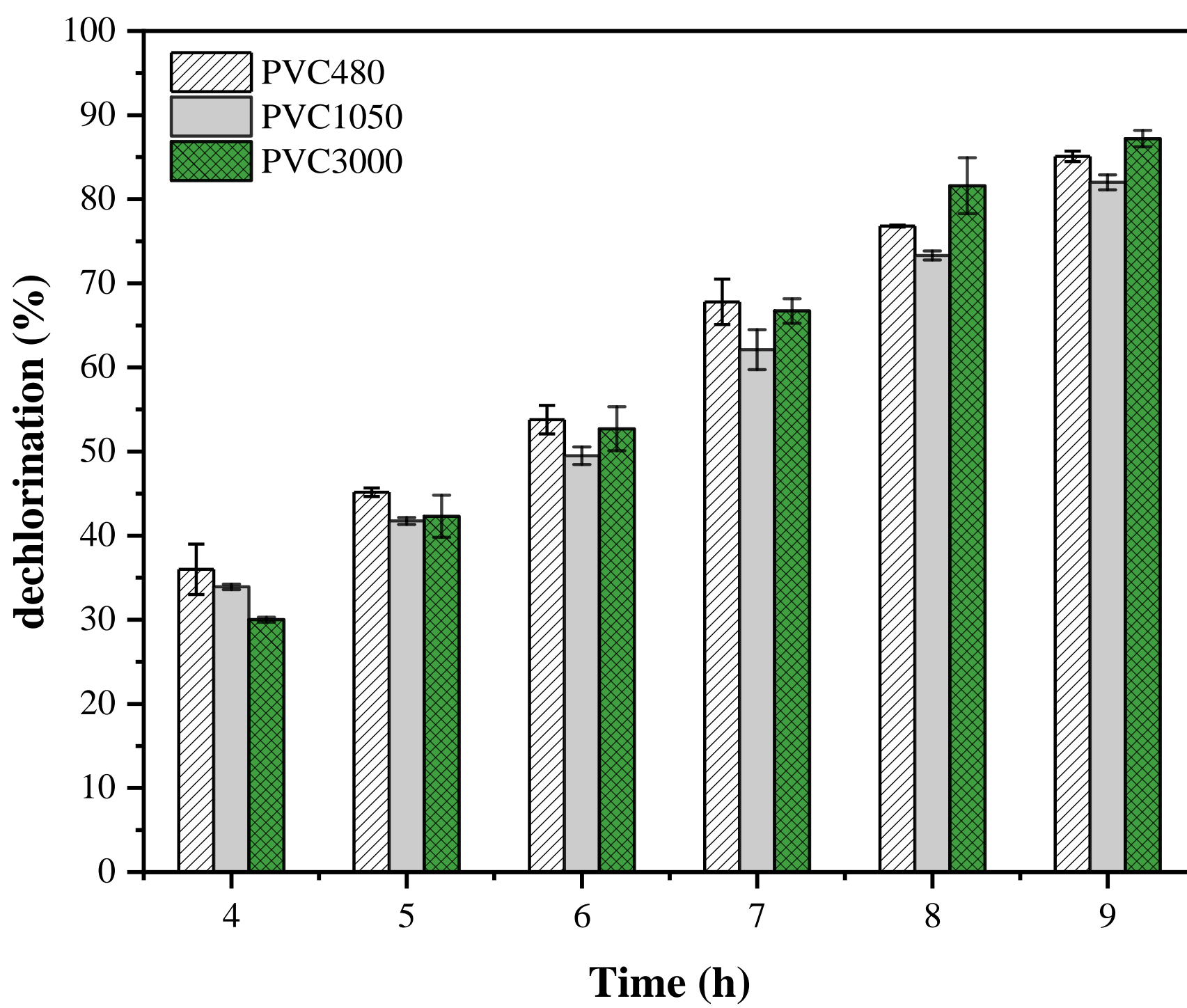
Thermal degradation of PVC with DP of 480, 1050, and 3000



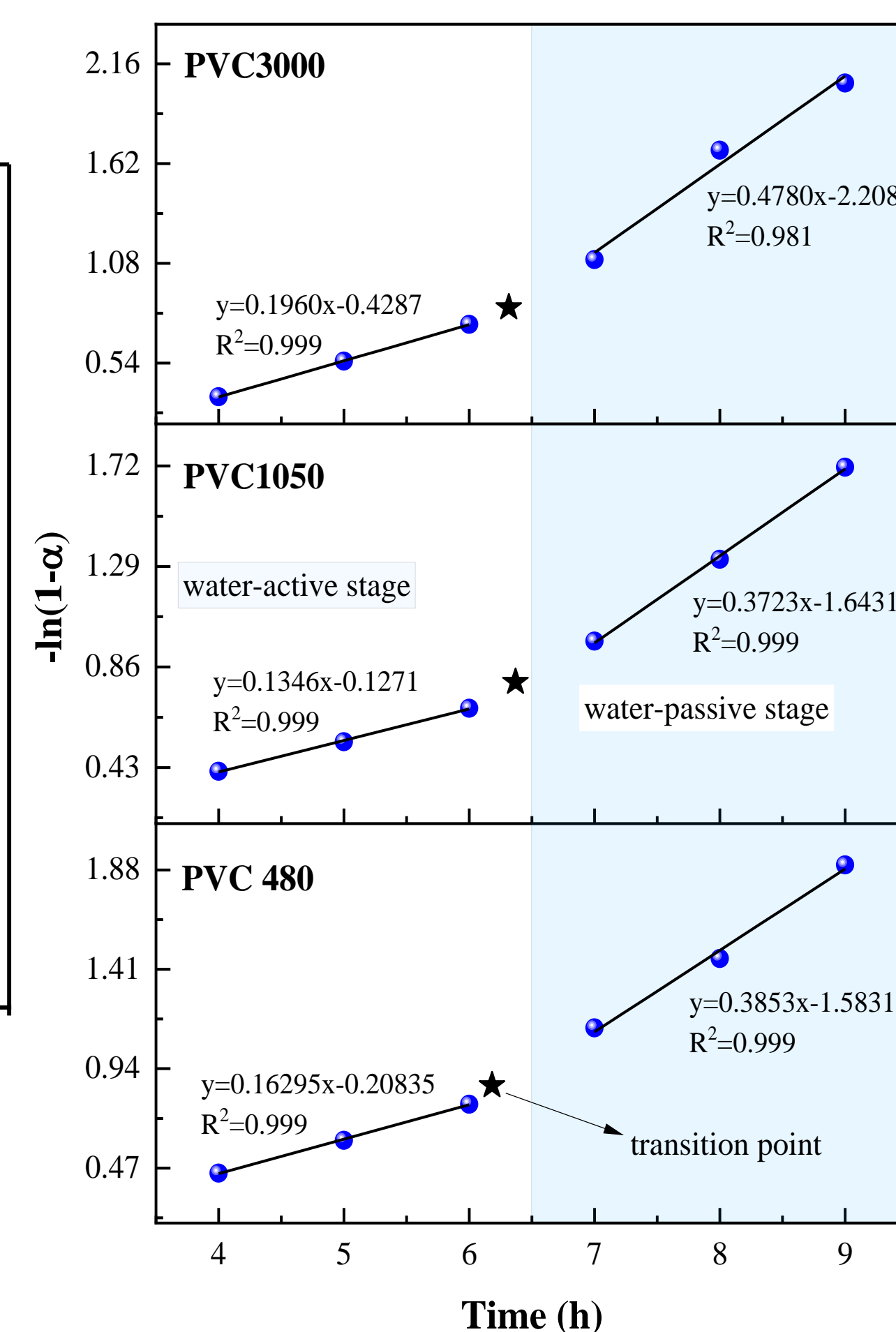
		PVC480	PVC1050	PVC3000
Stage 1	Peak Temp (°C)	286.9	288.6	291.8
	DTG (%/min ⁻¹)	16.37	15.10	18.24
	Area (units ²)	0.323	0.269	0.400
	DC ^a (%)	44.40	37.39	56.76
Stage 2	Peak Temp (°C)	312.8	309.5	311.7
	DTG (%/min ⁻¹)	4.574	4.760	3.180
	Area (units ²)	0.405	0.450	0.304
	DC (%)	55.60	62.61	43.24

Hydrothermal dechlorination of PVC with DP of 480, 1050, and 3000

Hydrothermal dechlorination with time

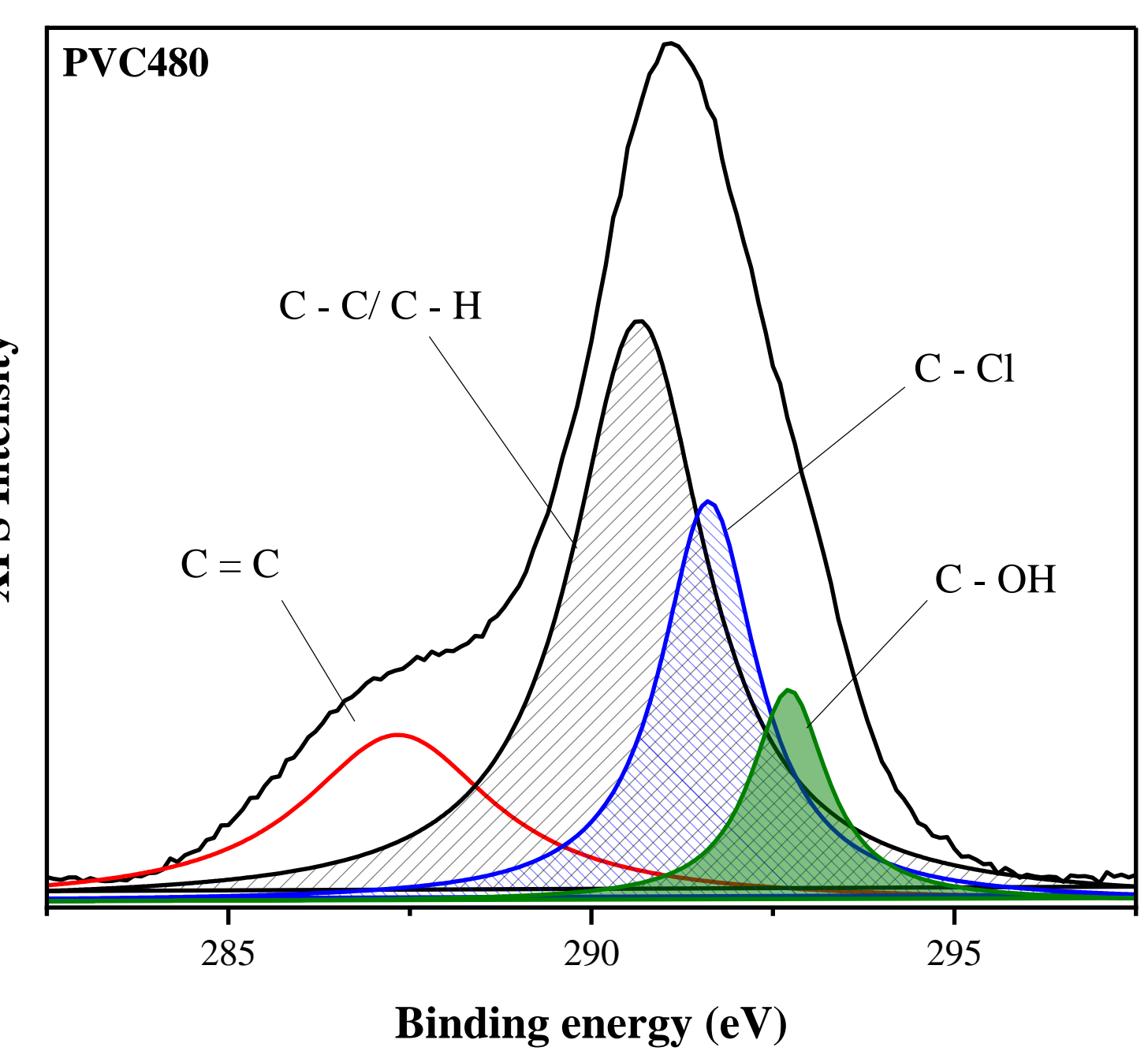
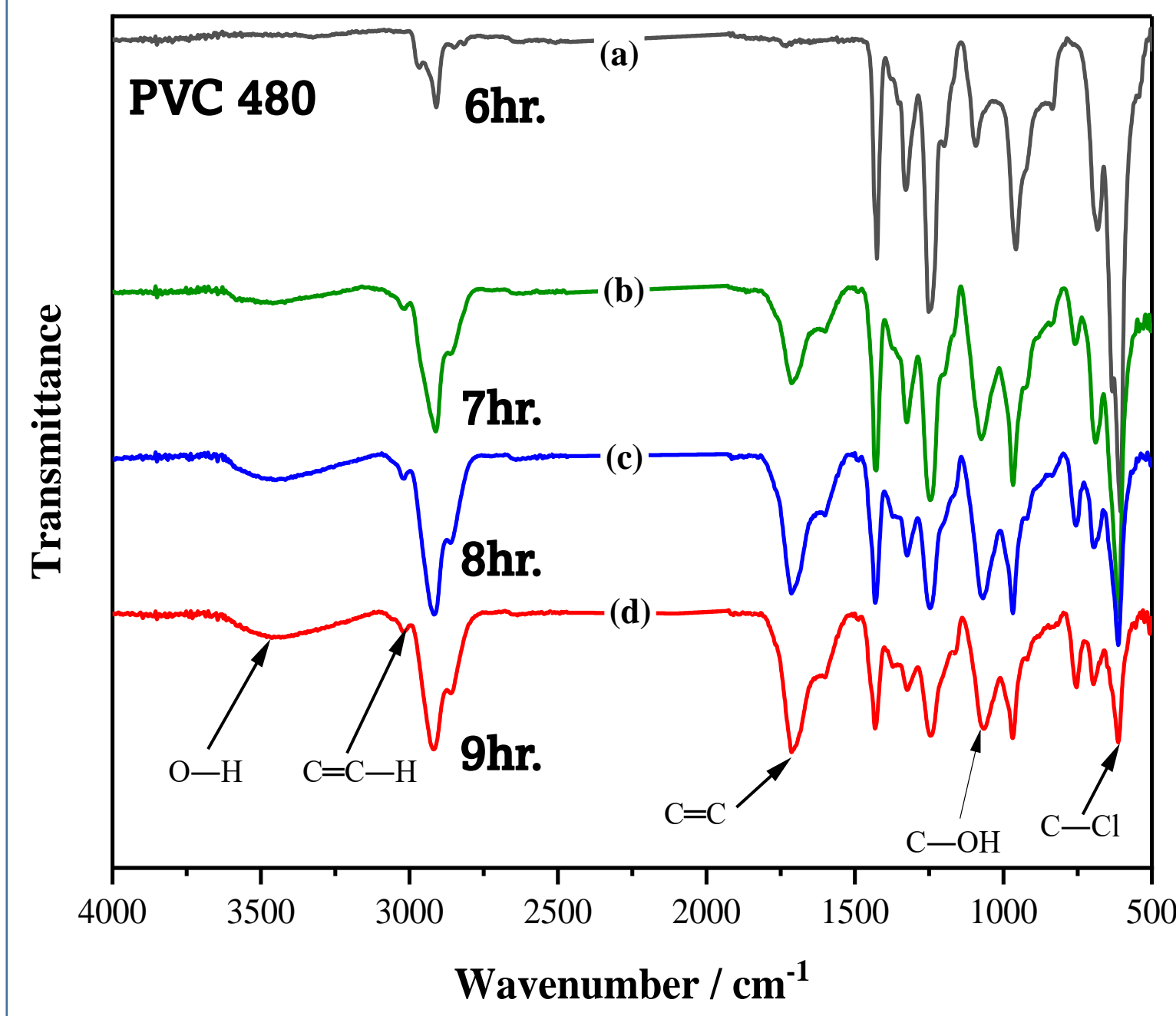


First-order plot



- Onset dechlorination depends on the thermal stability of the PVC
- PVC 3000 exhibits the highest reaction rate likely due to zipper mechanism propagation along chain length
- PVC 1050 is the lowest which is attributable to isomerization reaction and/or cyclization
- Hydrothermal dechlorination is a two-step process with a water active and passive stage

Characterization of PVC of typical semi-dechlorinated hydrochar (6hr)

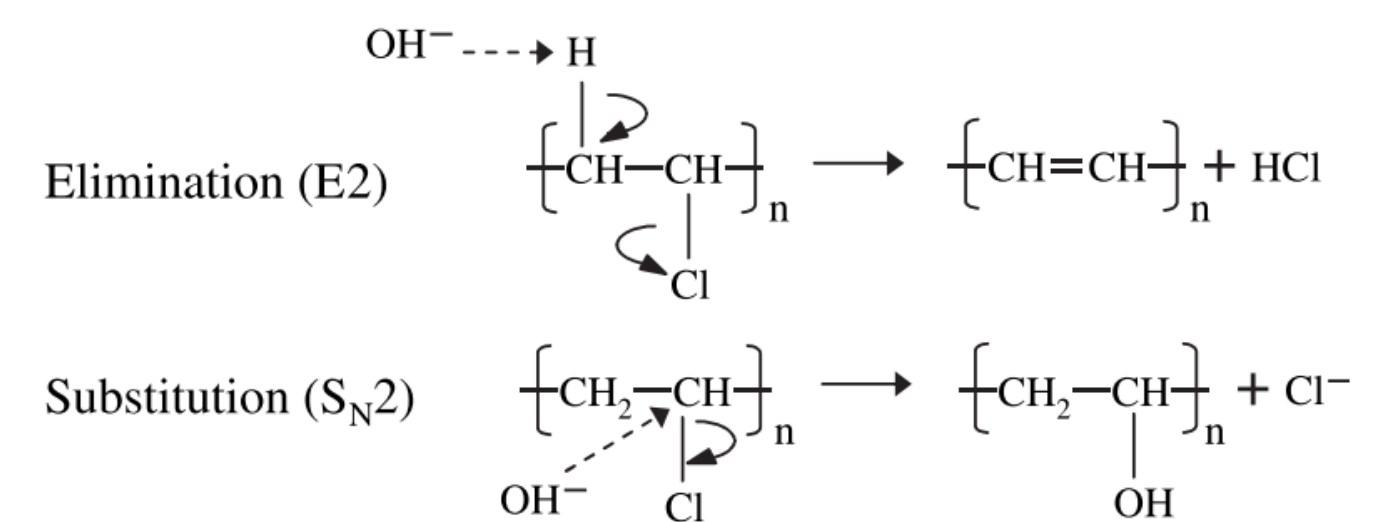
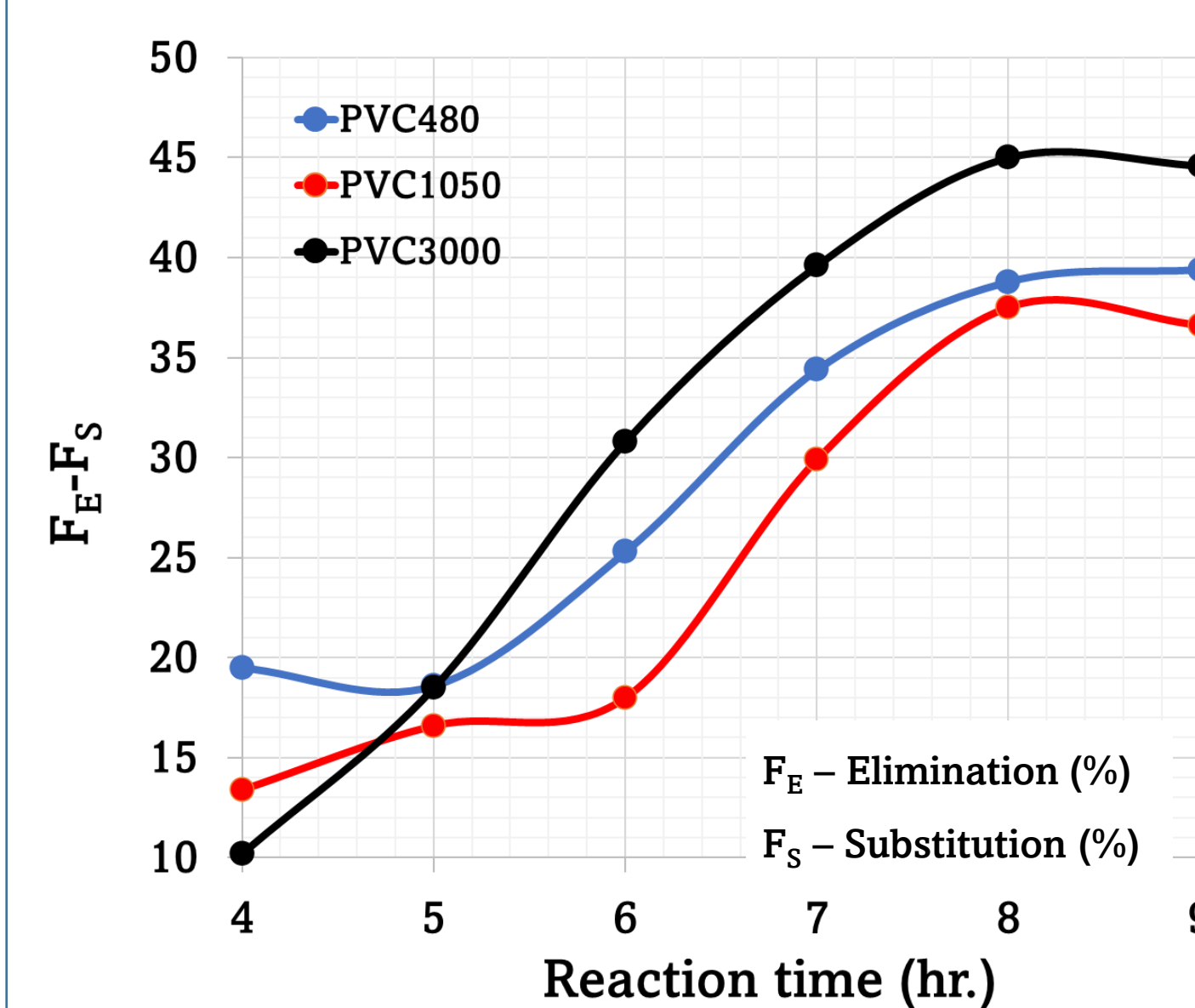


Deconvoluted XPS peak areas

Functional group	Binding energy eV	PVC480 %	PVC1050 %	PVC3000 %
C = C	287.5±0.28	19.36	15.85	22.98
C-C/C-H	289.5±1.22	47.41	34.00	38.51
C-Cl	290.4±1.28	23.40	34.53	28.30
C-OH	291.5±1.19	9.82	15.62	10.22

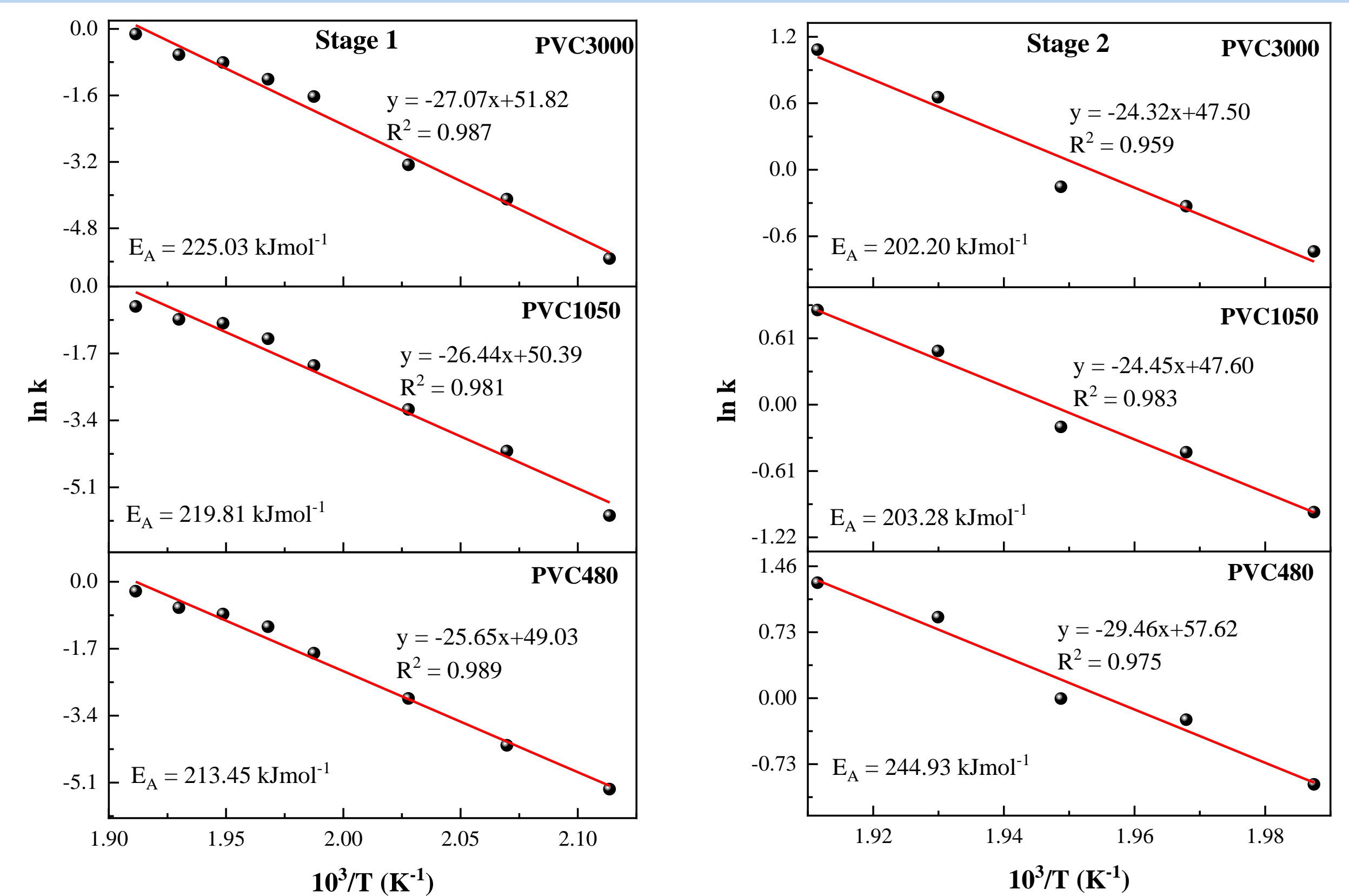
The mechanism is competitive elimination and nucleophilic substitution

Elimination and Substitution mechanism contribution



- Elimination reaction becomes prominent with an increase in conversion
- PVC3000 favors elimination compared to other DP
- Reaction is akin to the shrinking core model

Arrhenius Plots for different PVC polymers



Conclusions

- Contrary to convention, hydrothermal dechlorination is a two-stage process
- The stages can be classified as water-active and water-passive stage
- The activation energy for PVC480, PVC1050, and PVC3000 in the water-active stage are 213.45, 219.81 and 225 kJ/mol, respectively. And 244.93, 203.3, and 202 kJ/mol in the water-passive stage
- Elimination mechanism becomes more prominent with the dechlorination degree

Acknowledgments

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