Supporting Information

Sequential Reaction Control during *In-situ* Polymerization and Formation Processes of Reactive Polyurethane Coatings via Adjusting Molecular Weight and Isocyanate Content of the Prepolymer

Bin Zhao,[1,2] Huawei Xu,[3] Jie Liu,[3] Junfeng Zhang,[3] Huimin Duan,*[1,2,4] Peter Müller-Buschbaum,[5] Wengxin Chen,[1,2,4] Dongming Qi,*[1,2,4] and Qi Zhong*[1,2,4,5].

1. National Base for International Science and Technology Cooperation in Textiles and Consumer-Goods Chemistry & Zhejiang Provincial Engineering Research Center for Green and Low-Carbon Dyeing & Finishing Zhejiang Sci-Tech University Hangzhou 310018, P. R. China.

2. State Key Laboratory of Bio-based Fiber Materials, Zhejiang Sci-Tech University Hangzhou 310018, P. R. China.

3. Hexin Kuraray Micro Fiber (Haiyan) Co. Ltd., 383 Haihe Road, 314305 Jiaxing, China.

4. Zhejiang Provincial Innovation Center of Advanced Textile Technology, Shaoxing 312000, P.R. China.

5. Technical University of Munich, TUM School of Natural Sciences, Department of Physics, Chair for Functional Materials, James-Franck-Str. 1, 85748, Garching, Germany

Table S1. GPC data of different RPU coatings measured after initialization of reaction for 0, 5, 10, 15, 20, and 120 min.

Reaction Time(min)	Pre-SC/NCO-20	PDI	Pre-SC/NCO-24	PDI	Pre-LC/NCO-20	PDI	Pre-LC/NCO-24	PDI
0	4120	1.18	2397	1.34	9566	1.24	8789	1.27
5	10323	3.83	28655	4.38	17634	2.43	17750	2.19
10	12040	4.34	27483	4.32	20177	3.06	18677	2.70
15	17041	4.59	28282	4.37	20851	3.17	29429	4.27
20	19229	4.71	28100	4.20	22930	3.62	30116	4.08
120	23551	4.76	27907	4.05	23812	3.39	28124	4.06

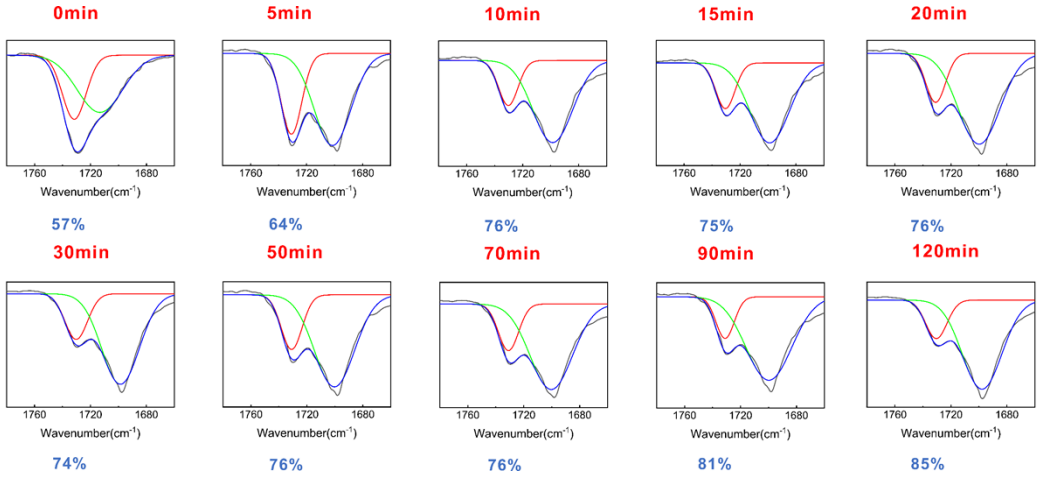

Figure S1. HBI from the C=O peak of Pre-SC/NCO-20 as a function of time during the *in-situ* polymerization and formation processes.

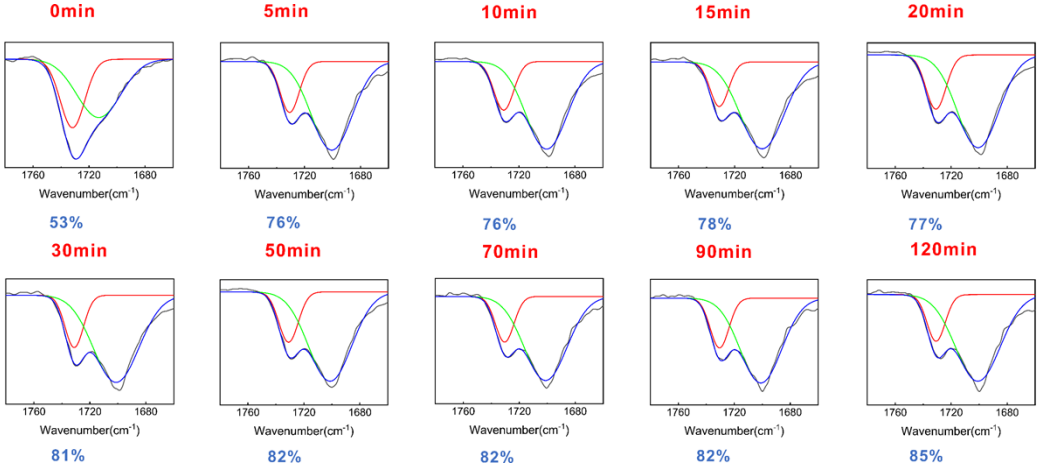

Figure S2. HBI from the C=O peak of Pre-SC/NCO-24 as a function of time during the *in-situ* polymerization and formation processes.

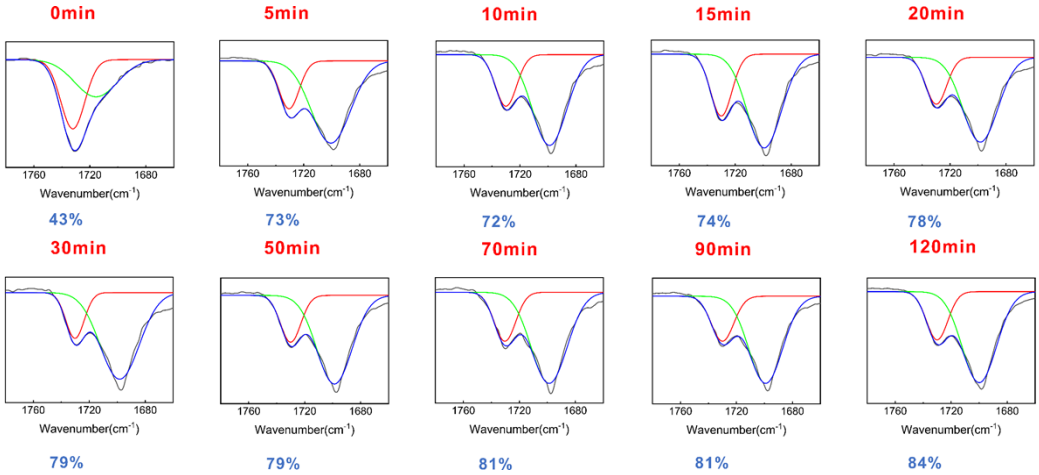

Figure S3. HBI from the C=O peak of Pre-LC/NCO-20 as a function of time during the *in-situ* polymerization and formation processes.

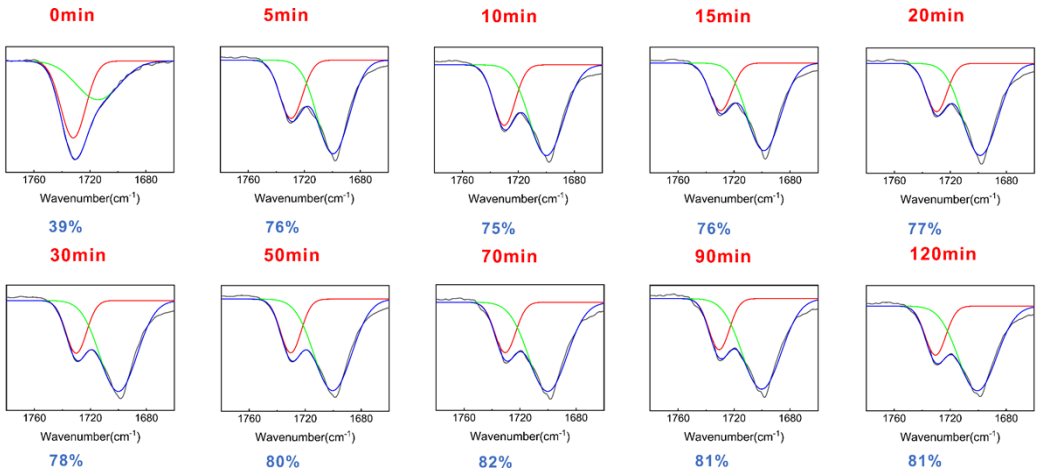

Figure S4. HBI from the C=O peak of Pre-LC/NCO-24 as a function of time during the *in-situ* polymerization and formation processes.

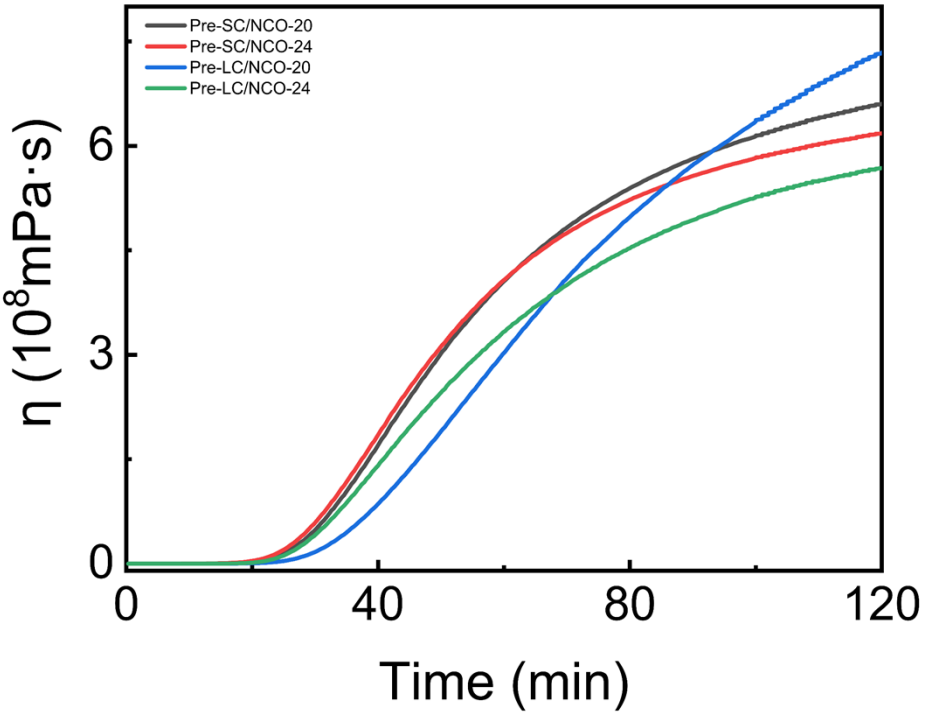

Figure S5. Complex viscosity (η) of the RPU coatings as a function of time during the *in-situ* polymerization and formation processes.

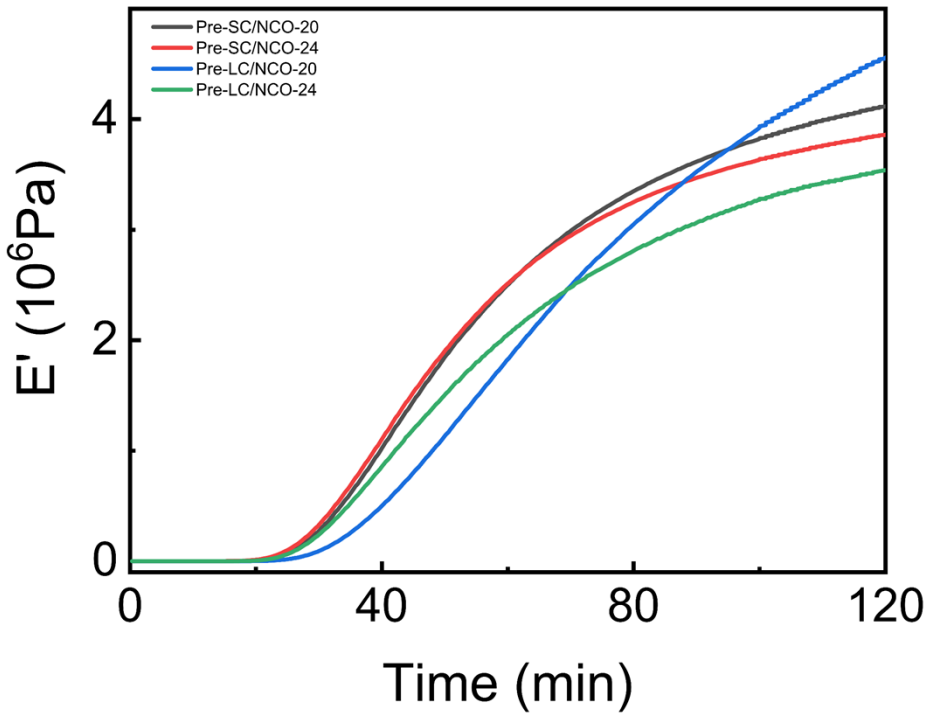

Figure S6. Storage modulus (E') of the RPU coatings as a function of time during the *in-situ* polymerization and formation processes.

The theoretical calculation formula for the free -NCO content in RPU prepolymer is as follows:

$$-NCO\% = \frac{\left[\left(\frac{0.98m_{MDI}}{M_{MDI}}\right) - n_{PTMEG} - 1.5n_{TMP}\right] \times 2M_{-NCO}}{m_{MDI} + m_{PTMEG} + m_{TMP}} \times 100\% \#(1)$$

$$m_{TMP} = \left(m_{MDI} + m_{PTMEG}\right) \times 2\% \#(2)$$

$$n_{TMP} = \frac{(m_{MDI} + m_{PTMEG}) \times 2\%}{M_{TMP}} \#(3)$$

in which the M_{-NCO} is 42.