

# Supplementary information for

## Forming of Nylon-6 Micro/nano-Fiber Assembly through a Low Energy Reactive Melt Spinning Process

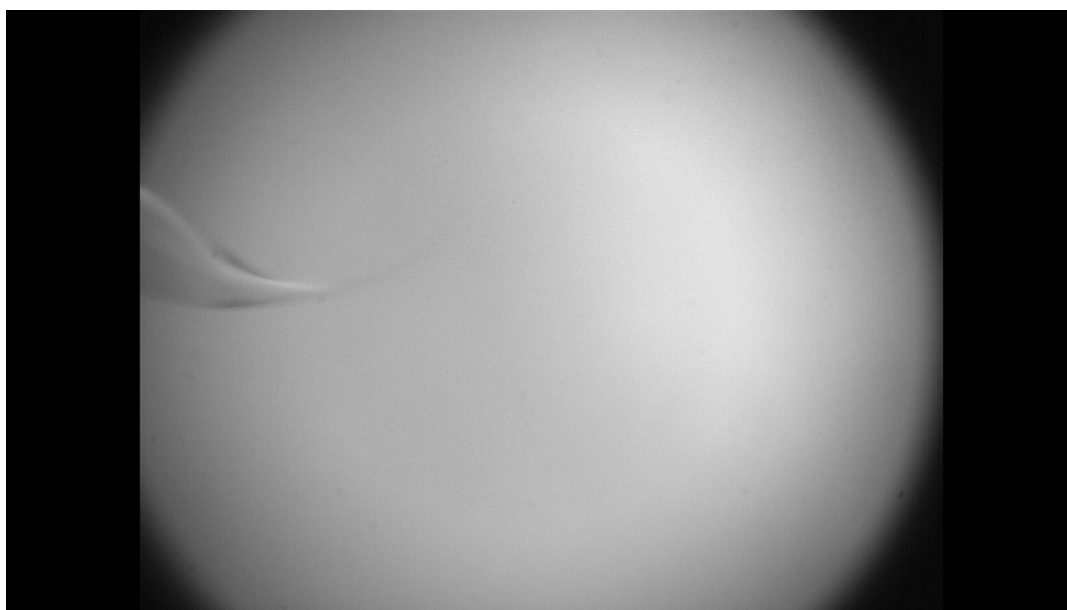
Renhai Zhao<sup>1</sup>, Xiao Meng<sup>1</sup>, Hongwei He<sup>1</sup>, Jinfa Ming<sup>1</sup>, Xin Ning<sup>1\*</sup>

Industrial Research Institute of Nonwovens & Technical Textiles, College of Textiles & Clothing, Shandong

Center for Engineered Nonwovens, Qingdao University, Qingdao 266071, China.

\*Corresponding author: [xning@qdu.edu.cn](mailto:xning@qdu.edu.cn) (X. N.); Tel.: +86-532-85953572.

### Supplementary Note 1 — High-speed videography of spinning process

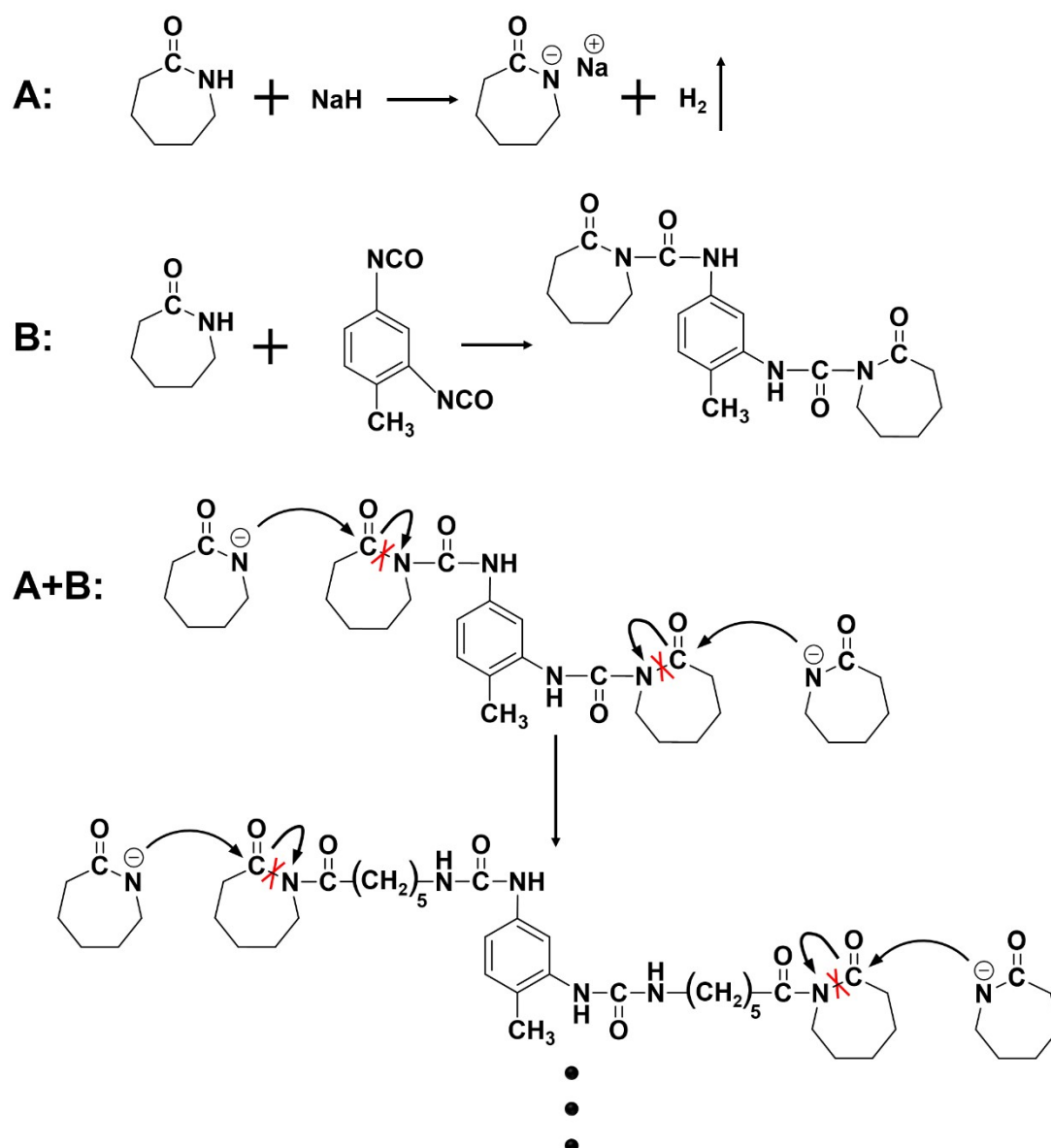


Supplementary Video 1. The direct observation of the continuous electrospinning process

To further monitor the continuity of the spinning process, a high-speed camera (iX Cameras i-SPEED 750, The United Kingdom) was used for the direct observation of the electrospinning process through the viewable window of spinning box (Fig. 1a). A continuous light illuminated the spinning area by a beam spot from a 250 W ultra-high brightness LED, which enabled the acquisition of clear images with a short exposure

time of the high-speed camera. The frame rate was 2,000 fps. As shown in Supplementary Video 1, due to the electric field induced stretching, a Taylor cone was formed from still polymerizing fluid mixture and thereby turned on a continuous spinning process.

## Supplementary Note 2— Ring-opening polymerization of caprolactam



Supplementary Figure 1. Reaction mechanism diagram of A and B components

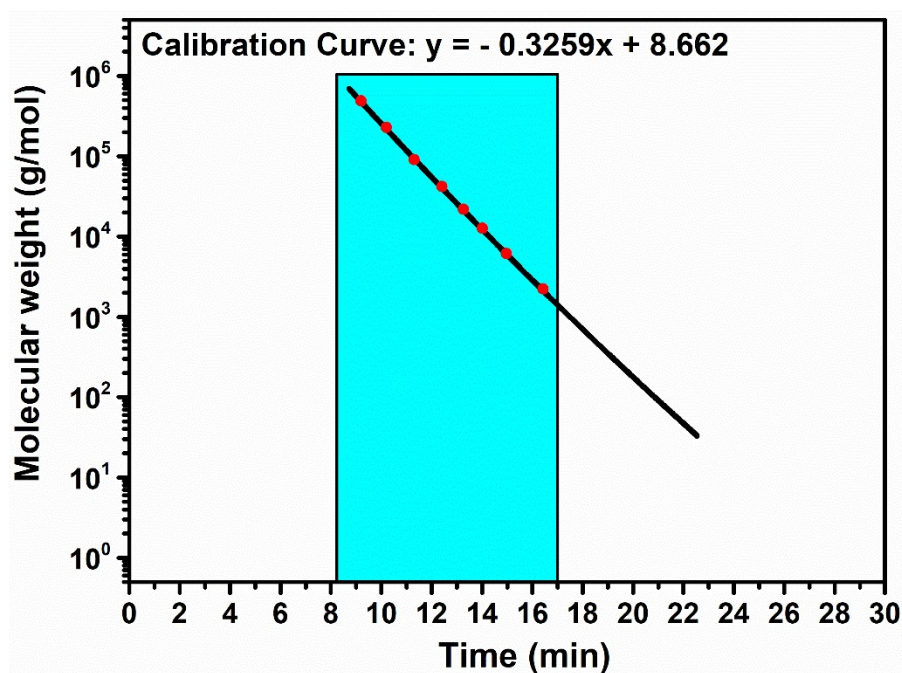
The rapid polymerization of nylon 6 requires the use of a catalyst-initiator system.

In the presence of catalyst and initiator, nylon 6 with high molecular weight can be produced by caprolactam (CL) anionic polymerization. Anionic polymerization of caprolactam with a high conversion rate in a few minutes, in which the catalyst can facilitate caprolactam anion generation and the initiator aims to form chain growth active center. In this research, the catalyst and initiator are each added to a separate stream to provide the required reaction control. The catalyst used was sodium caprolactam prepared by reacting anhydrous caprolactam with sodium hydride.

As shown in Supplementary Fig. 1, sodium hydride (NaH) attacks the weakly acidic N-H bond of CL and generates both a caprolactam anion and hydrogen. Blocked isocyanate is an adduct containing imide structure generated upon reacting toluene-2,4-diisocyanate (TDI) with a caprolactam containing an active hydrogen atom. Imide structure, as the active center of chain growth, reacts readily with caprolactam anion.

Subsequently, caprolactam anion attacked the caprolactam double-blocked isocyanate, and ring-opening reaction took place to generate another active anion. Then caprolactam reacted with the active anion to generate active caprolactam isocyanate, so as to realize chain growth. Subsequently, it was once more attacked by caprolactam anion to open the ring, thus continuously circulating, finally obtaining the polymer with required relative molecular weight.

### **Supplementary Note 3 — GPC calibration curve and data point**



Supplementary Figure 2. The molecular weight separation calibration curve

Supplementary Table 1. Column calibration data points

Point	Peak Max RT (min)	Log Mw	Mw (g/mol)
1	9.15000	5.72	524000
2	10.15000	5.34	217000
3	11.29667	4.95	88500
4	12.37333	4.62	41400
5	13.25667	4.36	22800
6	13.97000	4.11	12900
7	14.98000	3.78	5980
8	16.38000	3.33	2160

## Supplementary Note 4 — Caprolactam monomer conversion

Supplementary Table 2. The caprolactam monomer conversion rate of nylon-6 fibers at different

reactant proportion

Samples	CL monomer conversion rate			
	1	2	3	Average
93:7	85.3	82.3	80.5	82.7±2.4
94:6	82.9	87.3	88.3	86.2±2.9
95:5	90.6	93.8	91.9	92.1±1.6
96:4	89.9	93.3	94.2	92.5±2.3
97:3	94.3	95.6	96.5	95.5±1.1

Supplementary Table 3. The caprolactam monomer conversion rate of nylon-6 fibers at different

spinning temperatures

Samples	CL monomer conversion rate			
	1	2	3	Average
150	94.3	93.8	91.2	93.1±1.7
160	91.3	94.0	90.3	91.9±1.9
170	94.1	92.5	91.5	92.7±1.3
180	90.6	91.9	88.8	90.4±1.6
190	87.0	91.1	89.5	89.2±2.1