

# L-Lysine Functionalized Polyacrylonitrile Fiber: A Green and Efficient Catalyst for Knoevenagel Condensation in Water

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#### Abstract

The L-lysine functionalized polyacrylonitrile fiber ( $PAN_LF$ ) was prepared by grafting the L-lysine into a commercially available polyacrylonitrile fiber and showed highly catalytic activity for Knoevenagel condensation reaction. With low temperature (45 °C) and short reaction time (1 h), the fiber catalyst was well applicable to Knoevenagel condensation of a wide range of aldehydes and the yields could reach up to 99%. Interestingly, only in water could the reaction take place smoothly (with a yield of 88%) and a polar micro-environment promoted reaction process had been proposed to explain this phenomenon. Besides, the fiber catalyst has advantages of easy preparation, high functional degree, strong mechanical strength and thermal stability, etc. And it can be reused at least 5 times without further treatment and performed well in scaled-up experiment (amplified 50 times) and flow chemistry experiment (no loss of catalytic activity after 48 h), which indicates its potential application in industry application.

#### **Graphical Abstract**



Keywords Polyacrylonitrile fiber · L-Lysine · Supported catalyst · Knoevenagel condensation · Flow chemistry

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# 1 Introduction

Nowadays, more and more small organic molecules were used as catalysts instead of enzymes and metals to catalyze organic reactions [1]. Among them, amino acids including L-proline [2], phenylalanine [3], alanine and isovaline [4], as natural and environmentally benign compounds, have

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been demonstrated to be effective catalysts for many reactions, such as aldol reaction [3, 5], Mannich reaction [6, 7], Michael addition [8, 9], Knoevenagal condensation [10, 11] and so on [1, 12].

Knoevenagal condensation, which is the condensation of aldehydes or ketones with the compounds containing active methylene under the base catalysis to create  $\alpha,\beta$ -unsaturated carbonyl compounds and their analogues, is one of the most useful reactions in organic chemistry [13–19]. This reaction is environment-friendly because water acts as the by-product and it could proceed smoothly by the catalysis of ammonium salt [20], bases [21], amino acids [22], organometallics [23] and so on. What's more, microwave radiation [24], lipase [25] and ionic liquids [26, 27] were also used to promote the reaction. However, homogeneous catalysis will cause resource consumption and environmental pollution due to its intrinsic disadvantage of difficult separation of the catalyst.

Taking these into consideration, it was urgent to find a catalyst which could overcome these disadvantages and realize green chemical process. Thus, immobilized catalysts on solid materials which could be both eco-friendly and economic had attracted extensive attention. To synthesize them, a variety of solid materials have been used, such as silica gel [28], carbon materials [29, 30], metal oxides [31–34], zeolite [35], MCM [36, 37] and montmorillonite [38]. However, unsatisfactory catalyst loading, relatively higher temperature and complicated preparation process may be inevitable.

Polyacrylonitrile fiber (PANF) is a cheap commercial material with abundant cyano groups that could be easily transformed into amide, carboxyl or other functional groups [39–41]. Moreover, The PANF has excellent mechanical strength and flexibility which is very suitable for industrial application. In our previous reports, the PANF had been used as a supporter successfully to synthesize effective fiber catalysts for various organic reactions [42–44]. In this work, L-lysine was firstly immobilized onto the PANF and the obtained fiber catalyst could efficiently catalyze Knoevenagal condensation in water.

### 2 Experimental

### 2.1 Reagents

PANF was purchased from Fushun Petrochemical Corporation of China with the length of 10 cm and diameter of  $30 \pm 0.5$  mm. All reagents including aldehydes, ethyl cyanoacetate and organic solvents were analytical grade and were not purified before being used.

#### 2.2 Apparatus and Instruments

<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (101 MHz) spectra were recorded using CDCl<sub>3</sub> as a solvent and TMS as an internal standard on a Bruker Avance III (400 MHz) spectrometer. FT-IR spectra were obtained using a Bruker ALPHA spectrophotometer. Elemental analysis was obtained from an Elementar vario EL analyzer. Scanning electron microscope (SEM) (Hitachi, model S-4800) was used to characterize the surface of the modified fibers. Solar 969 Atomic Absorption Spectrometer (American Thermal Power Company) was employed to study the structure of the fiber catalyst. Melting points were acquired from a Yanagimoto MP-500 apparatus and were not corrected.

#### 2.3 Preparation of the Fiber Catalysts

L-Lysine (2.19 g, 15 mmol), anhydrous sodium carbonate (5.0 g), dried PANF (1.0 g) and deionized water (40 mL) were added into a three-necked flask and the mixture was stirred and refluxed for 13 h. Then the fiber was filtered out and washed with water (60–70 °C) until the filtrate was neutral. Finally, the modified fiber was dried overnight in vacuum at 60 °C to obtain the fiber catalyst.

### 2.4 General Procedure for Knoevenagel Condensation

A mixture of aldehyde (1 mmol), ethyl cyanoacetate (1.5 mmol), fiber catalyst (0.1 mmol) and 15 mL of deionized water or other solvents were put into a round-bottom flask. Then the mixture was stirred at 45 °C for 1 h. The fiber catalyst was filtered out and washed with ethyl acetate until no organic compounds were tested by TLC in the filtrate. The filtrates were combined, extracted three times with ethyl acetate, dried by anhydrous sodium sulfate and evaporated in vacuo. Finally column chromatography was performed to purify the product with petroleum ether-ethyl acetate as the eluent.

### 2.5 General Procedure for the Continual-Flow Process

The continual-flow reactor was prepared by filling  $PAN_LF$  (0.5 g) into a silicone tube with 0.5 cm inner diameter and 10 cm length. Then a solution of *p*-nitrobenzaldehyde (1 mmol/50 mL) and ethyl cyanoacetate (1.5 mmol/50 mL) in water/methanol (2:1) as solvent was pumped into the glass reactor at a rate of 0.05 mL/min at room temperature. After every 6 h, nitrobenzene as an internal standard was



Scheme 2 Possible mechanism of immobilizing H<sub>2</sub>N-R<sub>0</sub> on PANF

added to the effluent reaction solution, and the yield was determined by HPLC.

### **3** Results and Discussion

#### 3.1 Preparation of the Fiber Catalyst

Since the nucleophilic reactivity of two amino groups in L-lysine are almost identical [45, 46], there are two existing forms of  $PAN_LF$  (Scheme 1).

A possible mechanism of the immobilizing process is descripted in Scheme 2. Initially, the amino in  $H_2N-R_0$ attacked the C=N in PANF to form an intermediate I which turns to be intermediate II quickly. Then  $H_2O$  was added to C=NH in intermediate II and an intermediate III was formed. After releasing a molecule of NH<sub>3</sub>, the  $H_2N-R_0$  was immobilized on PANF.

The functional degree of the modified fiber was evaluated by the weight gain which was calculated by the equation below:

Weight gain =  $[(W_2 - W_1)W_1] \times 100\%$ 

in which  $W_1$  and  $W_2$  are the weights of PANF and the modified fiber, respectively.

The weight gain was influenced by the reflux time significantly. With the time prolonged from 10 to 14 h, the weight gain was increased from 4.5 to 18% (Table 1, Entries 1–5). However, it has a limitation because the mechanical strength of the fiber catalyst could be weakened by the increase of the weight gain. Taking this into consideration, we chose 13 h as the optimal reflux time. Besides, what we can see

Table 1 Effect of different reflux time on the weight gain of fiber

Entry	$Na_2CO_3(g)$	Time (h)	Weight gain (%)
1	5	10	4.5
2	5	11	8.6
3	5	12	12.5
4	5	13	15.4
5	5	14	18
6	_	22	_
7	_	44	_
8	_	48	5

General condition: PANF (1.0 g), L-lysine (2.19 g, 15 mmol),  $H_2O$  (40 mL) and anhydrous sodium carbonate (5 g or 0 g) were refluxed for appropriate time

from Table 1 is that sodium carbonate plays a significant role in the successful preparation of  $PAN_LF$ . Without sodium carbonate, we obtained no weigh gain even refluxing 44 h (Table 1, Entry 7). When the reflux time increased to 48 h, we only obtained a weight gain of 5% (Table 1, Entry 8), and the mechanical strength was too poor to use. Sodium carbonate was essential in this reaction because it can promote the hydrolysis of cyano groups in PANF, thereby facilitating the formation of amide bonds [47].

In order to determine the structure of the catalyst, we used AAS to determine the sodium ion content in the catalyst. The results were listed in the Table S1. As the PANF also contains sodium, we use the PANF as a blank control. After modification with L-lysine, the difference of sodium between  $PAN_{L}F$  and PANF is 0.23 mmol/g. And the theoretical value which refers to the increase of the sodium content when

PANF is functionalized with L-lysine in the presence of sodium carbonate is 0.25 mmol/g, which is almost consistent with the obtained data. Therefore, it is believed that our fiber catalyst is present as sodium salt (Scheme 1).

# 4 Characterization of the Fiber Catalyst

# 4.1 Elemental Analysis (EA)

The elemental analysis data of PANF, PAN<sub>L</sub>F and PAN<sub>L</sub>F-1 (acquired after the first use in the Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate) and PAN<sub>L</sub>F-5 (acquired after catalyzing 5 runs) are listed in Table S2. Compared to the original PANF, the carbon content and nitrogen content in PAN<sub>L</sub>F were significantly reduced while the hydrogen content increased as expected for the reason that L-lysine has less carbon, less nitrogen and more hydrogen than the original PANF.

After  $PAN_LF$  was used to catalyze Knoevenagel condensation for the first time, the carbon and hydrogen content were increased and the nitrogen content in  $PAN_LF$ -1 was reduced compared to PANF, which may be due to the adsorption of the intermediate or product on the fiber catalyst. Compared to  $PAN_LF$ -1, the carbon, hydrogen and nitrogen content in  $PAN_LF$ -5 had a slight increase since there may be some sodium ion loss.

### 4.2 SEM

The SEM images of PANF,  $PAN_LF$ ,  $PAN_LF-1$ ,  $PAN_LF-5$  are shown in Fig. 1. Compared to PANF,  $PAN_LF$  becomes thicker and its surface becomes slightly crude. The diameter of  $PAN_LF-1$  and  $PAN_LF-5$  have almost not changed and are only slightly greater than PANF, which indicates that the fiber catalyst was less damaged and could be reused in a relatively favorable state.



**Fig. 2** FT-IR spectra of *a* PANF, *b* PAN<sub>L</sub>F, *c* PAN<sub>L</sub>F-1, *d* PAN<sub>L</sub>F-5 and *e* L-lysine

Fig. 1 SEM images of a PANF, b PAN<sub>L</sub>F, c PAN<sub>L</sub>F-1, and d PAN<sub>1</sub>F-5



#### 4.3 FT-IR

Samples of PANF, PAN<sub>L</sub>F, PAN<sub>L</sub>F-1 and PAN<sub>L</sub>F-5 were pulverized by cutting and then prepared into KBr pellets. Their FT-IR spectra are shown in Fig. 2. The 2242  $\text{cm}^{-1}$ absorption band is attributed to C≡N vibrations and the absorption peak at 1732 cm<sup>-1</sup> is the stretching vibration absorption peak of C=O in the ester group, and its presence proves the presence of the second monomer methyl acrylate in the PANF (Fig. 2a). After grafting the L-lysine, the 2243 and 1732 cm<sup>-1</sup> peaks are slightly weakened (Fig. 2b), which indicated that a portion of  $C \equiv N$  and  $CO_2Me$  have participated in the amidation and the hydrolysis. For PAN<sub>I</sub>F, the new broad absorption band near 3455 cm<sup>-1</sup> belongs to the stretching vibrations of the N-H groups. Another new strong peak appears at 1673 cm<sup>-1</sup> corresponds to the stretching vibration of C=O in the amide. In addition, the peak at 1655 cm<sup>-1</sup> is assigned to the stretching vibration of C=O in L-lysine (Fig. 2e), which indicate the success immobilization of the L-lysine. After the first run, PAN<sub>I</sub> F-1 (Fig. 2c) almost showed the same FT-IR Spectrum as PAN<sub>I</sub> F (Fig. 2b) except a slight weakening at 1655 cm<sup>-1</sup>. After fifth run, the peak at 1655 cm<sup>-1</sup> becomes weaker, which indicates the slight L-lysine loss during the reaction process.

#### 4.4 X-Ray Photoelectron Spectroscopy (XPS)

The XPS spectra of PANF and PAN<sub>L</sub>F are shown in Fig. 3. For PANF, peaks at 1073.6, 499.2 and 64.8 eV could be assigned to the characteristic binding energies of Na(I) (Fig. 3a) [48–50]. This demonstrates the existence of sodium 4-vinylbenzenesulfonate. After being modified by L-lysine, peaks at 1072.6, 499.2 and 64.8 eV are enhanced distinctly (Fig. 3b), which shows the successful immobilization of L-lysine in its sodium salt formation. After being reused



Fig. 3 XPS spectra of a PANF, b PAN<sub>L</sub>F, c PAN<sub>L</sub>F-5

five times, the characteristic peaks of Na(I) were weakened which might be due to the partial loss of Na<sup>+</sup>.

#### 4.5 XRD

The structures of different fibers were also characterized by XRD (Figrue 4). The peaks at  $2\theta = 16.9^{\circ}$  and  $29.5^{\circ}$  in spectrum of PANF correspond to the strong diffraction of (100) face and weak diffraction of (110) face, respectively (Fig. 4a). For spectrum of PAN<sub>L</sub>F, the peak at  $2\theta = 17^{\circ}$  is weaker than that of PANF, which indicates that the skeleton structures of the fiber have been slightly damaged during the modifying process. After being used five times in Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate, the peak at  $2\theta = 17^{\circ}$  is much weaker. However, the skeleton structure of the fiber is reserved.

#### 4.6 Thermogravimetric Analysis

The TG/DSC curves of PANF and PAN<sub>L</sub>F are given in Figure S1 and Fig. 5, respectively. The maximum thermal decomposition temperature ( $DSC_{max}$ ) of the PANF was determined to be 309.4 °C (Figure S1). After being modified by L-lysine, the  $DSC_{max}$  of PAN<sub>L</sub>F was declined to 298.6 °C (Fig. 5), which shows that the structure of the fiber was only destroyed slightly and the PAN<sub>L</sub>F has the similar thermal stability to PANF.

#### 4.7 Mechanical Experiment

A fiber catalyst with higher mechanical strength will be more suitable for its application as fixed bed material in industry. The mechanical properties of PANF and  $PAN_LF$  have been tested and the results are shown in Table 2. Compare to the



Fig. 4 XRD spectra of a PANF, b PAN<sub>I</sub>F, c PAN<sub>I</sub>F-5



Fig. 5 TG/DSC curves of PANF

original PANF (its break strength is 11.0 cN), break strength of the  $PAN_LF$  is declined to 6.8 cN (Table S3, entries 1, 2). That was caused by a certain extent of destroy to fiber structure at high temperature. After being used once and five times, because of the mild reaction conditions the breaking

Table 2 Optimization of the Knoevenagel condensation

strength of the PANLF-1 only slightly declined to 6.7 and 6.4 cN, respectively (Table S3, entries 3, 4). Besides, from the SEM images of PAN<sub>L</sub>F-1 and PAN<sub>L</sub>F-5 (Fig. 1c, d) we can see that the basic fiber skeleton had not been damaged, which also shows the well physical and chemical stability of the fiber catalyst during the catalytic process.

### 5 Application of L-lysine Functionalized PANF in Knoevenagel Condensation

#### 5.1 Catalytic Activity

We examined the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate using the L-lysine functioned PANF as the catalyst. Primarily, we conducted two blank experiments. In one experiment, only water was added as the solvent and no catalyst was used; another involved PANF as the catalyst. As expected, the yield of the former was only 9% (Fig. 6), and the latter was 12% (Fig. 6). When L-lysine was used as the catalyst, we obtained a yield of 33% (Fig. 6). However, our fiber catalyst could obtain a yield of 63% (Fig. 6).



Entry	Solvent	Temp (°C)	Reactant ratio	Yield <sup>a</sup> (%)
1	Water	0	1:1	32
2	Water	25	1:1	64
3	Water	35	1:1	68
4	Water	45	1:1	77
5	Water	55	1:1	77
6	Water	75	1:1	77
7	Water	95	1:1	71
8	Methanol	45	1:1	16
9	Acetonitrile	45	1:1	0
10	1,4-Dioxane	45	1:1	0
11	Ethanol	45	1:1	5
12	Ethyl acetate	45	1:1	0
13	Toluene	45	1:1	0
14	Water	45	1:1.25	82
15	Water	45	1:1.5	88
16	Water	45	1:1.75	90
17	Water	45	1:2	88

Reaction conditions: benzaldehyde (1 mmol), ethyl cyanoacetate,  $PAN_LF$  (10 mol%) in each solvent (15 mL) for 1 h <sup>a</sup>Obtained yield by HPLC



Fig. 6 The catalytic activities of PANF, L-lysine and  $PAN_LF$  in catalyzing Knoevenagel condensation

### 5.2 Optimization of the Knoeveagel Condensation Conditions

We chose the condensation of benzaldehyde and ethyl cyanoacetate as a model reaction to optimize the reaction conditions. First, we studied the influence of reaction time. When the time was increased from 5 min to 2 h, the yield was improved in 1 h and nearly stabilized from 1 to 2 h (Fig. 7a). Then, the catalyst amount was taken into consideration. From 2.5 to 10 mol%, the yield was increased. However, the yield was nearly constant from 10 to 20 mol% (Fig. 7b).

Additionally, we also investigated reaction temperature. From 0 to 45 °C, the yield continued to rise and it was nearly unchanged when the temperature was raised from 45 to 95 °C (Table 2, Entries 1–7). Besides, different solvents were used to test the effect of solvents on Knoevenagel condensation when PAN<sub>I</sub>F acted as the catalyst. As we can see from the Table 2 (Entries 4, 8–13), the polarities of solvents have significant impacts on the reaction yields. We could obtain a higher yield of 77% if a highly polar solvent like water was used (Table 2, Entry 4). When the polarity of the solvent was reduced and methanol was used, a low yield of 16% was got (Table 2, Entry 8). And with the use of less polar solvents, such as acetonitrile, 1,4-dioxane, ethanol, ethyl acetate and toluene, the reaction could not occur effectively (Table 2, Entries 9–13). This phenomenon can be explained by the relative polarity of the surface of PAN<sub>I</sub>F, reactants, and solvent. A highly polar micro-environment promotion process has been proposed to make this phenomenon easy to understand (Figure S2). The PAN<sub>I</sub> F with highly polar surface micro-environment can't be infiltrated well and constrictive in weak polar solvents, the low polar organic reactants are well dissolved in weak polar solvents (Figure S2a), and hardly access to the active catalytic sits in the high polar micro-environment of the fiber catalyst. The PAN<sub>I</sub>F was infiltrated well in high polar solvent like water, and it's surface micro-environment was unfolded (Figure S2b). On the other hand, low polar reactants can hardly dissolve in water and are compelled to adhere on the surface of fiber catalyst. In this way, the reactants can access to the microenvironment of the PAN<sub>I</sub>F and be catalyzed by active catalytic sites to generate the product. It is specific and favorable highlight for PAN<sub>I</sub>F with high selectivity to strong polar solvents (especially for water, which is an environmentally friendly solvent).

What's more, in order to increase the yield, we tried to change the proportion of reactants, namely increase the amount of ethyl cyanoacetate. When the ratio of benzaldehyde to ethyl cyanoacetate was 1:1.25, the yield was increased to 82% (Table 2, Entry 14). A higher yield of 88%



Fig. 7 Effects of a reaction time and b catalyst amount on the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate





was obtained when the ratio reached 1:1.5 (Table 2, Entry 15). The yield was nearly constant even the amount of ethyl cyanoacetate was improved to 1.75 or 2 equiv. (Table 2, Entries 16–17) In a word, the acquired optimum reaction conditions were: aldehyde to ethyl cyanoacetate 1:1.5, 15 mL of water, 10 mol% of catalyst dosage, 45 °C, 1 h.

### 5.3 Possible Mechanism of the Knoevenagel Reaction

A possible mechanism of the Knoevenagel reaction catalyzed by  $PAN_LF$  is shown in Scheme 3. Initially, the  $PAN_LF$ removes an  $\alpha$ -proton from ethyl cyanoacetate to generate a carbanion  $A^-$  and the lysine moiety on  $PAN_LF$  exists as an inner salt. Then carbanion  $A^-$  attacks the carbonyl carbon of aldehyde to form an intermediate **C** which then captures a proton from  $PAN_LF$  to produce an intermediate **D**. After an intramolecular dehydration of **D**, the  $\alpha,\beta$ -unsaturated carbonyl compounds were released and the fiber catalyst was recovered to promote the next reaction cycle.

### 5.4 Knoevenagel Condensation of Various Aldehydes with Ethyl Cyanoacetate

Under the optimized conditions, the Knoevenagel condensation of different aldehydes with ethyl cyanoacetate was studied. The results of the experiments are shown in the Table 3. When the aromatic ring does not have any substituent (benzaldehyde), the yield was 81% (Table 3, Entry 1). The electron withdrawing groups in aromatic rings can reduce the electronic cloud density of carbonyl carbon atom, increase its electrophilicity and increase the reactivity of the aldehyde. Therefore, when the aromatic ring contains strong electron-withdrawing groups such as nitro, trifluoromethyl, the yield can reach more than 95% (Table 3, Entries 2-4). For o-nitrobenzaldehyde, it was even up to 99%. o-Chloro, o-bromo and p-chlorobenzaldehyde also obtained high yields (Table 3, Entries 5–7). In contrast, when an electron-donating group was attached to the aromatic ring, the activity of the aldehyde carbonyl was weakened and the yield decreased (Table 3, Entries 8–10). However, o-methoxybenzaldehyde still gave 85% yield (Table 3, Entry 11). For some aldehydes with heterocycles, such as furan formaldehyde and thiophene formaldehyde, PAN<sub>I</sub> F also has a good catalytic effect on them, providing 99% and 91% yields, respectively (Table 3, Entries 12-13). Aliphatic aldehyde like 3-cyclohexenylformaldehyde could also give a yield of 85% (Table 3, Entry 14). The superior results suggest that the PAN<sub>I</sub> F is a highly active catalyst for the Knoevenagel condensation in water. Because of the high activity of the malononitrile, the reaction of malononitrile with different aldehydes can be finished at RT with yields of 97-99%. However, the reaction of benzaldehyde with acetylacetone only obtained a yield of 36% due to the low activity of the acetylacetone. After refluxing 6 h, no product was detected for the ethyl 2-cyanopropanoate, which indicates that steric hindrance has great influence on the reactivity of the substrate.

Entry	1	2	Product		Yield $(\%)^a$
1	CHO		CN CN COOC <sub>2</sub> H <sub>5</sub>	3a	81
2	CHO		COOC <sub>2</sub> H <sub>5</sub>	3b	99
3	CHO O <sub>2</sub> N		O <sub>2</sub> N CN CN	3c	96
4	CF <sub>3</sub> CHO		CF <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	3d	95
5	CI		CI COOC <sub>2</sub> H <sub>5</sub> CN	3e	93
6	CI		Cl CN COOC <sub>2</sub> H <sub>5</sub>	3f	81
7	Br		Br COOC <sub>2</sub> H <sub>5</sub>	3g	88
8	СНО		COOC <sub>2</sub> H <sub>5</sub>	3h	66
9	H <sub>3</sub> CO CHO		H <sub>3</sub> CO	3i	50
10	H <sub>3</sub> CO CHO		H <sub>3</sub> CO CN	3ј	76
11	OCH3 CHO		OCH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	3k	85
12	CHO CHO		COOC <sub>2</sub> H <sub>5</sub>	31	99
13	S CHO		S COOC <sub>2</sub> H <sub>5</sub>	3m	91
14	СНО		CN CN	3n	85
15°	СНО	NCCN		30	98
16 <sup>b</sup>	H <sub>3</sub> CO CHO	NC CN	H <sub>3</sub> CO <sup>CN</sup>	3р	98
17 <sup>b</sup>	CI	NC CN	CI CN	3q	97
18 <sup>b</sup>	O <sub>2</sub> N CHO	NCCN	O <sub>2</sub> N CN CN	3r	99
19 <sup>c</sup>	СНО			3s	36
20 <sup>d</sup>	СНО		OH COOC <sub>2</sub> H <sub>5</sub>	3t	0

 Table 3
 Reaction of aldehydes with methylele active compounds

#### Table 3 (continued)

Reactions were carried out with benzaldehyde (1 mmol), ethyl cyanoacetate (1.5 mmol), 15 mL water in the presence of 10 mol% PAN<sub>L</sub>F under 45 °C in 1 h <sup>a</sup>Isolate yield by column chromatography <sup>b</sup>At RT for 1 h <sup>c</sup>At 80 °C for 6 h <sup>d</sup>Refluxed for 6 h

### 5.5 Reusability of the Catalyst PAN<sub>L</sub>F

The recyclability of the fiber catalyst  $PAN_LF$  was tested by catalyzing the Knoevenagel condensation of benzaldehyde (1 mmol) and ethyl cyanoacetate (1.5 mmol) in water (15 mL) at 45 °C. After the completion of each cycle, the fiber catalyst was taken out and then washed with ethyl acetate to remove the adsorbed reagents. The recycled catalyst was dried and reused directly in the next cycle without any additional treatment. The obtained yields of the first five cycles were 81, 80, 73, 62 and 60%, respectively, which indicated that the  $PAN_LF$  could be reused at least five times.

### 5.6 Comparison of PAN<sub>L</sub>F with Other Catalysts

Hexamethylenediamine aminated fiber  $(PAN_HF)$  and L-Lysine functionalized graphene oxide  $(GO_L)$  were prepared similarly to catalyze the Knoevenagel condensation, respectively. The reaction conditions were: benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), 15 mL water 10 mol % PAN\_LF, 45 °C and 1 h. We obtained yields of 55% (PAN\_HF) and 39% (GO\_L), respectively, which were lower than that of PAN\_LF (77%). Obviously, our catalyst PAN\_LF has better catalytic effect.

### 5.7 Scaled-Up Experiment of the Knoevenagel Condensation Catalyzed by PAN<sub>L</sub>F

Under the optimized conditions, the Knoevenagel condensation was scaled up by 50 times and the reaction can smoothly undergo with a yield of 88% in 1 h, which indicated that the  $PAN_LF$  had a potential application in industry.

### 5.8 Flow Chemistry of the Knoevenagel Reaction Catalyzed by PAN<sub>L</sub>F

Furthermore, in order to study the potential application of the fiber catalyst in industry.  $PAN_LF$  was employed in a simple continual-flow reactor by filling  $PAN_LF$  into a silicone tube and the Knoevenagel condensation reaction was used as a template reaction to test the continual-flow reaction (Fig. 8). A solution of *p*-nitrobenzaldehyde and ethyl cyanoacetate was pumped into the silicone reactor at 45 °C



Fig. 8 Schematic diagram of the continual-flow reaction system

and the results are shown in Figure S3. After 48 h, the yield of the Knoevenagel condensation reaction was basically unchanged, which indicates high potential application of this fiber catalyst in industry.

# **6** Conclusions

In summary, L-lysine functionalized polyacrylonitrile fiber has been designed and synthesized. As a heterogeneous catalyst, it was used to catalyze the Knoevenagel condensation of various aldehydes and ethyl cyanoacetate highly efficiently to afford the corresponding  $\alpha$ ,  $\beta$ -unsaturated cyanoesters. The fiber catalyst has advantages of easy preparation, high functionality degree, strong mechanical strength and thermal stability, etc. After optimization, with water as the solvent, a high weight gain, good strength and high catalytic activity fiber catalyst was obtained. When it was used to catalyze the Knoevenagel condensation, the catalyst had a high selectivity with water as the solvent, which met the requirements of green chemistry. A series of aldehydes reacted smoothly with cyanoacetate under the catalysis of PAN<sub>I</sub> F to afford the corresponding products in moderate to excellent yields from 50 to 99%. The catalyst could be easily separated from the reaction system and reused at least five times without any other treatment. It also performs well in scaled-up and flow

chemistry experiments, which have potential applications in industry.

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