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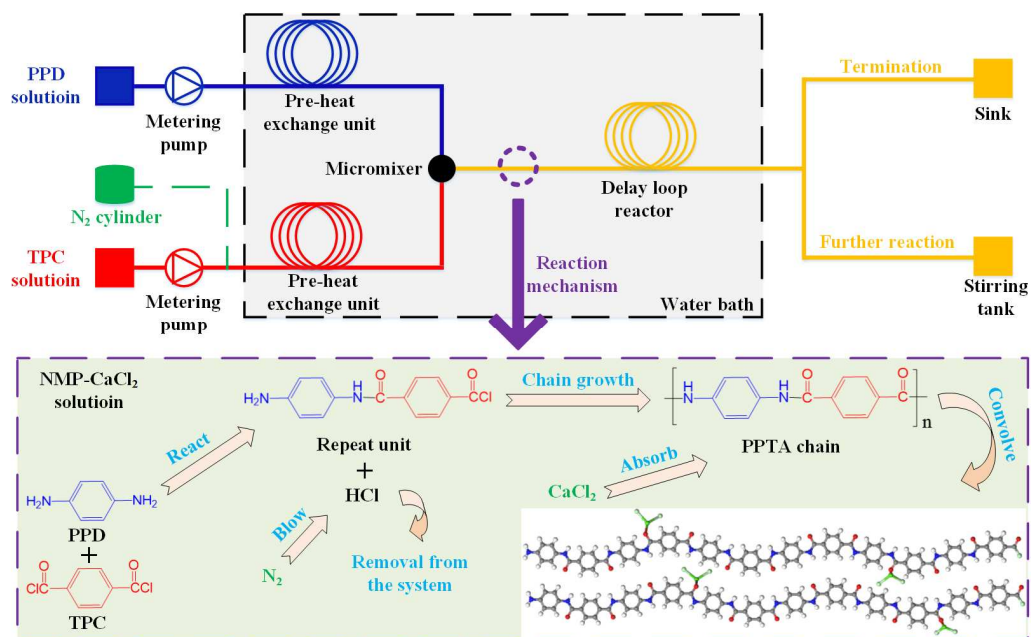
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Graphical abstract:



PPTA was prepared in a microstructured chemical system, and the apparent polycondensation kinetics was studied.



Journal Name

ARTICLE

## Preparation of poly(*p*-phenylene terephthalamide) in a microstructured chemical system

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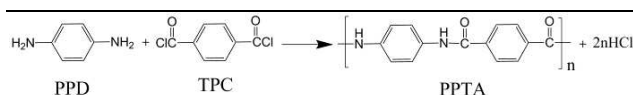
[www.rsc.org/](http://www.rsc.org/)Peijian Wang,<sup>a</sup> Kai Wang,<sup>a†</sup> Jisong Zhang,<sup>a</sup> Guangsheng Luo<sup>a†</sup>

A microstructured chemical system, mainly including a micro-sieve mixer, a delay loop and a stirring tank, was designed to implement the polycondensation of *p*-phenylenediamine (PPD) and terephthaloyl chloride (TPC) for the preparation of poly(*p*-phenylene terephthalamide) (PPTA). A two-step method was exhibited, which consisted of fast conversion of more than 90% reactive groups in the delay loop and further chain growth in the stirring tank. This new polycondensation method had several advantages, such as continuous operation at higher temperature and out of pyridine, which made the process more controllable and environmentally friendly. PPTA particles with weight-average molecular weight ( $M_w$ ) from 4,000 to 16,000 were obtained at different synthesis conditions, and their structures were characterized by XRD, POM, IR, EA and SEM. The apparent reaction kinetics in the delay loop was also studied, which showed that the apparent activation energy was 12 kJ/mol with a pre-exponential factor of  $5.4 \times 10^3$  L/(mol·s).

### Introduction

PPTA is a kind of aromatic polyamides with excellent performances in tensile property, toughness, weight, corrosion resistance, thermal and dimensional stability.<sup>1</sup> As a result, commercial fibers based on PPTA, such as Kevlar, Twaron, Technora, etc., have been widely used in composite reinforcement, ballistic resistance, ropes and cables, asbestos replacement and so on.<sup>2</sup> Therefore it comes with no surprise that research and publications on the preparation of PPTA are growing fast during recent years.<sup>3,4</sup> Morgan et al. reported an interfacial polycondensation method, in which PPTA film formed at the interface of the aqueous phase (containing PPD) and organic phase (containing TPC) after they were mixed.<sup>5</sup> Hyunykook et al. proposed a vapor polycondensation method.<sup>6</sup> Gaseous aromatic diacyl-chloride and aromatic diamine

reacted in the presence of tertiary amine and inert gas and PPTA was obtained after removing HCl from the reaction system. Fukuji et al. reported a direct polycondensation.<sup>7-9</sup> Aromatic diacyl-chloride and aromatic diamine reacted with each other in an organic solvent, such as N-methyl-2-pyrrolidone (NMP) or dimethylacetamide (DMAC), with the presence of triphenyl phosphite acting as a catalyst and pyridine working as the HCl absorbent. Also a facile synthetic route to PPTA with dual functional groups was proposed by Du et al. via the Claisen rearrangement reaction.<sup>10,11</sup>

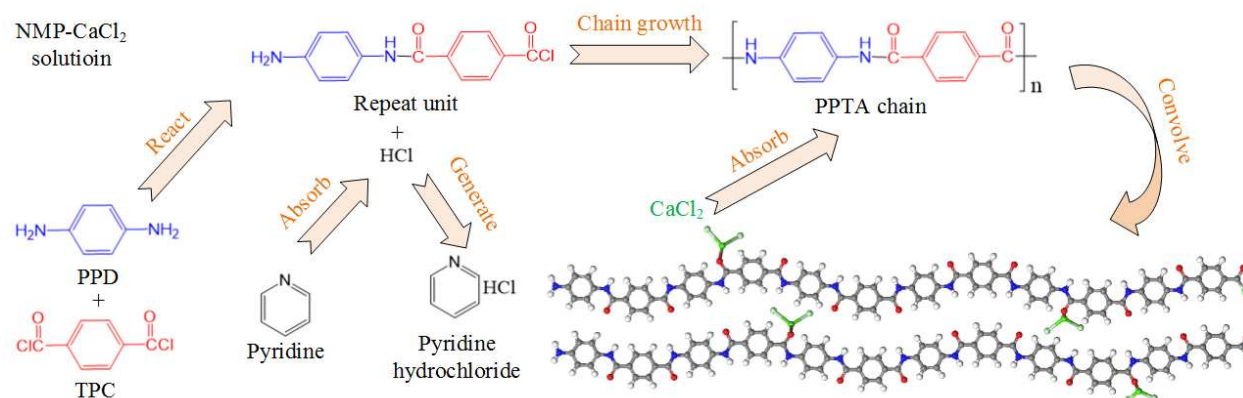


**Scheme 1** Polycondensation of PPD and TPC for the preparation of PPTA.

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## ARTICLE



**Fig 1.** Schematic diagram for the low temperature method.

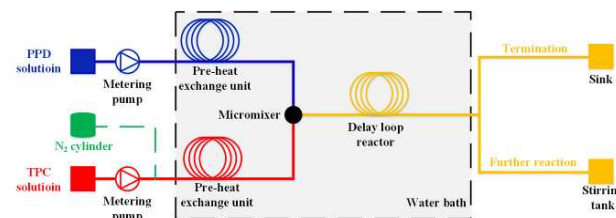
Besides these novel synthesis methods mentioned above, the traditional synthesis process of PPTA is a low temperature polycondensation reaction, which involves PPD and TPC in a mixed solvent of NMP contained CaCl<sub>2</sub>, shown in Scheme 1 and Figure 1.<sup>12</sup> In this cooling polycondensation process, the mixture viscosity increases rapidly as the molecular weight grows, resulting in strong difficulty in reactant mixing. Because of the high activity of the monomers, this process requires strict isolation of oxygen and water. Pyridine is necessary on the absorption of HCl because of its alkaline effect, avoiding the undesired interaction between HCl and PPD. CaCl<sub>2</sub> is used to weaken the hydrogen bond interaction between PPTA chains because of the complexation between calcium ion and amidogen. What's more, since the polycondensation is very rapid and strongly exothermic (reaction enthalpy is -107 kJ/mol),<sup>13</sup> an efficient heat exchange system is needed when a traditional reactor is applied.

According to the above characteristics of the polycondensation reaction to prepare PPTA, the microstructured chemical system, which contained a micromixer, high efficient heat exchangers and also a delay loop, is considered to be a more efficient device to realize the polycondensation process of PPD and TPC. First of all, the characterized dimension of a micromixer is usually smaller than one millimeter, which largely shortens the molecule diffusion distance<sup>14</sup> and contributes to a highly efficient mixing ability. Secondly, the heat-transfer coefficient in a microreactor can be as high as 54,000 W/(m<sup>2</sup>·K),<sup>15</sup> due to its much larger surface-to-volume ratio than the traditional stirring reactor.<sup>16</sup> Thus, the reaction heat can be removed quickly and temperature would be well controlled. Plenty of researches have been done for the application of microstructured chemical system in polymerization process in recent years.<sup>17-19</sup> For example,

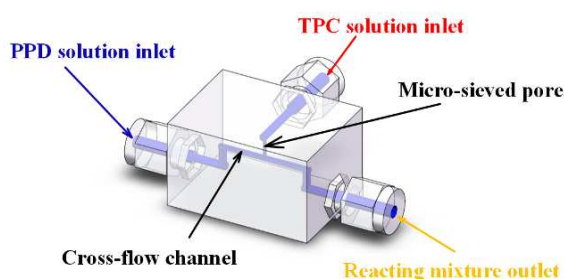
Kuboyama et al. carried out the polycondensation process of 4,4'-oxydianiline and isophthaloyl dichloride in a flow microreactor system. The polymerization reaction in their microstructured system was found faster than that in a traditional batch reactor, owing to a higher mixing efficiency of monomers.<sup>20</sup>

Based on these considerations, we proceeded the polycondensation of PPTA in a self-made microstructured chemical system in this study. The system was mainly organized by a micro-sieve mixer to mix the reactants, a metal delay loop for heat exchange and a stirring tank to quench or finish the reaction process. Higher temperature range (0 ~ 80 °C) than that in the classical synthesis of PPTA was tested, which is good for reducing the interaction between HCl and PPD and the viscosity of reacting mixture. Our previous work has shown that high mixing efficiency could be achieved in a microstructured chemical system, resulting in most PPD reacting with TPC directly, and only a small amount of PPD would combine with HCl. What's more, the high temperature in this study would promote the separation of PPD and HCl.<sup>21</sup> Under such condition, the toxic pyridine is not considered in this study. Instead, inert N<sub>2</sub> is used to act as the desorption media of HCl, making the process more environmentally friendly. The continuous feeding system, the small micromixer and the delay tube provided a perfectly sealed environment, which kept the reactants away from water and oxygen in atmosphere. Last but not least, the residence time in the microstructured system can be regulated by changing the length of the tube or varying the flow rate, which provides the basis of the apparent kinetics study of the polycondensation process.<sup>22</sup> By taking advantages of all these merits of microstructured chemical system, PPTA with good quality was obtained through the self-constructed microstructured

chemical system. To determine the optimal conditions for PPTA synthesis, the effects of a number of factors on the  $M_w$  of PPTA were investigated. Further, the polycondensation kinetics was also studied to provide more general information and deeper understanding of the process, which is crucial for developing and optimizing this new process.



**Fig. 2** The schematic overview of the microstructured chemical system.



**Fig. 3** The structure and appearance of the micro-sieve mixer.

## EXPERIMENTAL

### The microstructured chemical system

The schematic diagram of the microstructured chemical system designed to carry out the polycondensation of PPTA is shown in Figure 2. In this system the PPD/NMP-CaCl<sub>2</sub> solution and TPC/NMP-CaCl<sub>2</sub> solution were delivered to the pre-heating loops by metering pumps (Beijing Satellite Co., Ltd.). The loop tubes ( $d_{in} = 2$  mm) joined with each other at a micro-sieve mixer, whose structure is shown in Figure 3. In this micromixer, the TPC solution passed through a squared micro-sieved pore ( $a = 0.2$  mm) and then mixed with the PPD solution in a cross-flow channel ( $l \times w \times h = 12 \text{ mm} \times 0.4 \text{ mm} \times 0.6 \text{ mm}$ ). Replaceable delay loops ( $d_{in} = 2$  or 3 mm) were placed downstream of the mixer to provide changeable residence time of the reaction. The pre-heating loops, the micro-sieve mixer and the delay loops were all made from 316L stainless steel and they were immersed in a water bath to keep the temperature constant. The polycondensation process could be terminated instantly once the reacting mixture was fed into a tank contained room temperature water, so that reacting performance at different residence time can be studied. The reacting mixture could also be pumped into a tank with strong stirrer (Wiggins Labortechnik GmbH Germany) to further conduct the reaction process. When using the gas agitation method, N<sub>2</sub> was mixed into the TPC solution using a tube joint and the flow rate of N<sub>2</sub> was controlled by a mass flowmeter (Sevenstar Co., Ltd.).

### Materials and analysis

PPD (>99%), TPC (>99%), NMP (>99%) and CaH<sub>2</sub> (>95%) were purchased from J&K Scientific Ltd. (Beijing). 4A Molecular sieve, CaCl<sub>2</sub> (>96%) and ethanol (>99%) were provided by Beijing Chemical Works. The trace water in NMP was removed by adding in molecular sieve and CaH<sub>2</sub> before the experiments, avoiding the hydrolysis of TPC by H<sub>2</sub>O in NMP. Water content in NMP after this treatment is  $49.1 \pm 9.7$  mg/kg, measured using a moisture-testing instrument (Mettler Toledo, Switzerland). The highest possible average molecular weight was explained in the supporting material, considering the hydrolysis of TPC with H<sub>2</sub>O. Besides, the TPC/NMP solution was prepared just before the experiments, normally in less than 10 minutes, to avoid the potential reaction between TPC and NMP.<sup>23</sup> To eliminate the O<sub>2</sub> dissolved in NMP, N<sub>2</sub> was brought in to bubble in the solvent. CaCl<sub>2</sub> was heated at 400 °C for 4 hours to dehydrate before used. PPD/NMP-CaCl<sub>2</sub> solution and TPC/NMP-CaCl<sub>2</sub> solution with specific concentration were prepared in volumetric flasks before experiments. After the reaction, the PPTA product was washed with deionized water and then immersed in ethanol for 8 hours. Finally, the PPTA particles were dried at 120 °C for 12 hours before characterization.

### Characterization

The inherent viscosity method is a standard method adapted by many literatures to measure the molecular weight of polymers, thus we also use this method to measure the molecular weight of PPTA product. In the experiments, the inherent viscosity of PPTA-sulfuric acid solution at the concentration of 0.5 g/dL ( $5 \text{ kg/m}^3$ ) was tested. The relationship between the weight-average molecular weight of PPTA ( $M_w$ ) and the inherent viscosity<sup>2</sup> is:

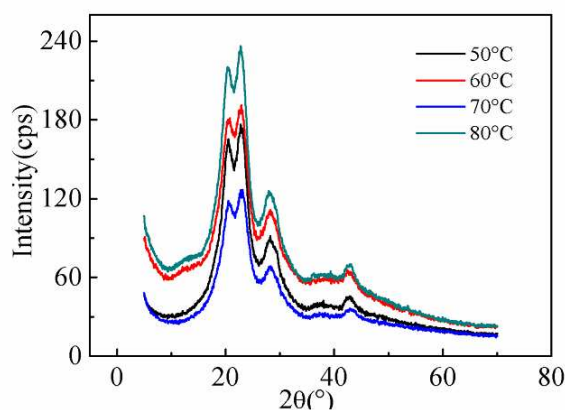
$$M_w = 3902.4 \cdot \eta_{inh}^{1.556} \quad (1)$$

To further evaluate the overall quality of the PPTA product synthesized by the newly designed microstructured chemical system, X-ray diffraction (XRD), polarizing optical microscopy (POM), infrared spectrum (IR), scanning electron microscope (SEM) and elemental analysis (EA) were also applied to characterize the product. Specifically, XRD (max-RB, Rigaku Corporation Japan) was used to characterize the crystal structure of PPTA product. POM (OLYMPUS BX41 Japan with a Moticam Pro camera) was used to characterize the liquid crystalline behaviour of the anisotropic PPTA/H<sub>2</sub>SO<sub>4</sub> solution. A Fourier transform infrared spectrometer (SENSOR 27, Bruker Optics Instruments Company Germany) was applied for IR analysis of the chemical bond and the macroscopic view of the product were observed using a SEM (JSM-7401, JEOL Ltd Japan). In addition, an elemental analyzer (VARIO EL III, Elemental Analysis Systems Company Germany) was used to measure the nitrogen, carbon, hydrogen and oxygen element contents in PPTA product.

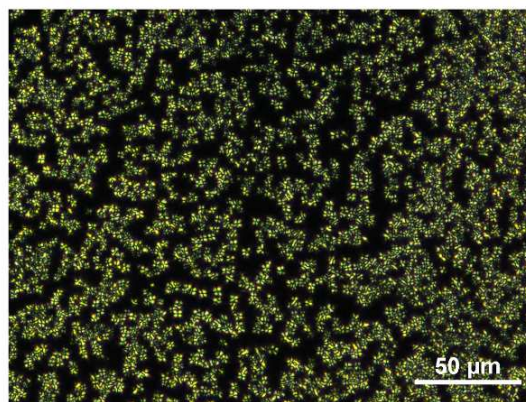
## RESULTS AND DISCUSSION

### Product Characterization

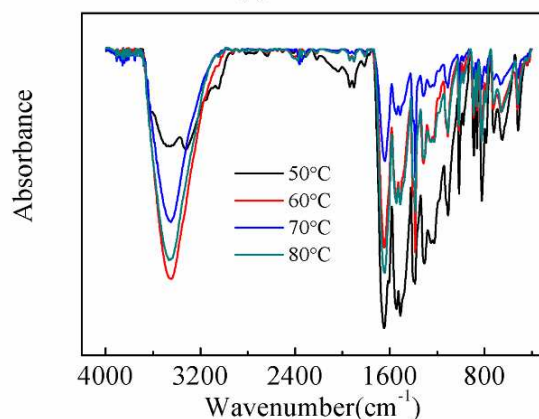




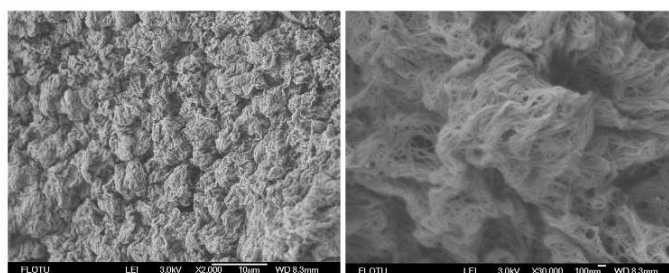
(a) XRD



(b) POM



(c) IR



(d) SEM

**Fig. 4** Characterization results of PPTA products: (a) XRD; (b) POM; (c) IR; (d) SEM. Experimental conditions:  $C_{\text{PPD}} = 0.100$  mol/L,  $C_{\text{TPC}} = 0.102$  mol/L,  $T = 50 \sim 80$  °C, delay loop  $d_{\text{in}} = 3$  mm,  $L_t = 2$  m,  $F_{\text{PPD}} = 20$  mL/min,  $F_{\text{TPC}} = 20$  mL/min. The reaction was quenched at the outlet of the loop. Samples for POM and SEM testing were prepared at 70 °C. Concentration of the PPTA/H<sub>2</sub>SO<sub>4</sub> solution for POM testing was 10wt %.

**TABLE 1** Element analysis of PPTA product.

Elements	N	C	H	O	C/N
Theoretical value	11.76	70.59	4.20	13.45	6.00
50 °C	11.36	69.12	4.28	15.24	6.08
60 °C	11.42	68.96	4.28	15.34	6.04
70 °C	11.40	69.23	4.26	15.11	6.07
80 °C	11.45	69.14	4.37	15.04	6.04

The characterization results of PPTA are shown in Figure 4 and Table 1. Figure 4 (a) gives the XRD results of the samples

prepared under different temperature. 20.5°, 23.0° and 29.0° are diffraction peaks of 110, 200, 004 crystal faces in PPTA, which is consistent with previous literature.<sup>24</sup> The typical POM result of the experimental product is shown in Figure 4 (b), indicating the anisotropic PPTA/H<sub>2</sub>SO<sub>4</sub> solution exhibits liquid crystalline behaviour. This result also coincides with the description in literature.<sup>2</sup> The IR results are shown in Figure 4 (c). The absorption band at 1640 cm<sup>-1</sup>, which is called amide I band, is caused by the stretching vibration of C=O. Absorption bands at 1540 cm<sup>-1</sup> and 1260 cm<sup>-1</sup>, indicating amide II band and amide III band respectively, are caused by the deformation coupling vibrations of O=C-N and N-H. Again, these IR spectrum results are consistent with those has been

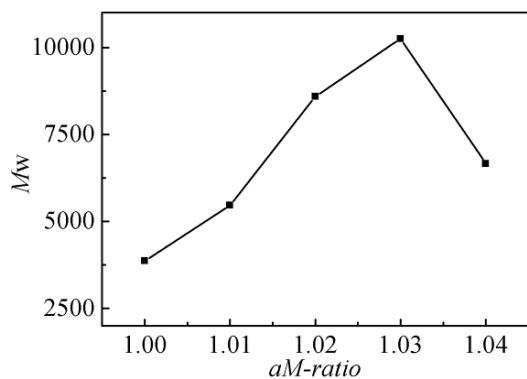
reported.<sup>25</sup> The SEM results of the samples are shown in Figure 4 (d). The particle size of PPTA products is about dozens of micrometers, and the PPTA chain strips could be observed clearly.<sup>26</sup> Table 1 shows the EA results of PPTA samples prepared at different temperature. Considering the error of EA equipment (1%), the amounts of N, C, H and O are basically consistent with the theoretical values.

#### Molecular weight of PPTA at the loop outlet

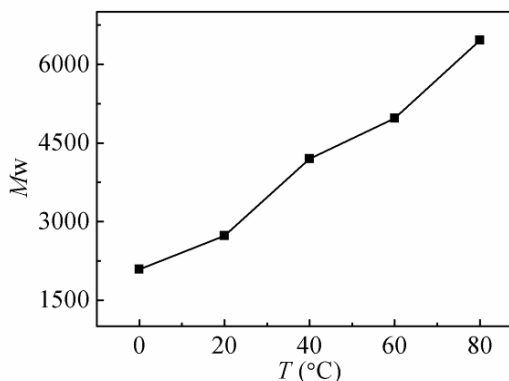
**Effects of apparent molar ratio of TPC/PPD.** In the polycondensation process of two different monomers, molar ratio of the monomers is one of the most important factors determining the average molecular weight of the final polymer. A little excess of one monomer would lead both ends of polymer chains to be occupied by the same monomer, preventing further increase of molecular weight. Theoretical equation for calculating the degree of polymerization from molar ratio is as follows:<sup>27</sup>

$$\bar{X}_n = \frac{1+r}{1+r-2rP} \quad (2)$$

where,  $\bar{X}_n$  is the degree of polymerization;  $r$  is the molar ratio of the two monomers whose range is between 0 to 1;  $P$  is the extent of functional groups that have participated in the reaction. Based on Equation (2), the highest molecular weight could only be got when the molar ratio of the two monomers is exactly 1. However, the optimized apparent molar ratio of TPC/PPD ( $aM$ -ratio) shows a little deviation from 1 because of errors from monomer purity, pump metering flow rates and other non-ideal situations in the experiments. Effects of  $aM$ -ratio on the  $M_w$  of PPTA is shown in Figure 5. The  $aM$ -ratio was changed by adjusting the concentration of TPC while keeping PPD concentration constant at 0.200 mol/L. The relatively optimal  $aM$ -ratio was found to be between 1.02 and 1.03 in the present experiment.



**Fig. 5** Effect of  $aM$ -ratio on the  $M_w$  of PPTA. Experimental conditions:  $C_{PPD} = 0.200$  mol/L,  $C_{TPC} = 0.200 \sim 0.208$  mol/L,  $T = 40$  °C, delay loop  $d_{in} = 2$  mm,  $L_t = 6$  m,  $F_{PPD} = 20$  mL/min,  $F_{TPC} = 20$  mL/min. The reaction was quenched at the outlet of the loop.



**Fig. 6** Effect of temperature on the  $M_w$  of PPTA. Experimental conditions:  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 0 \sim 80$  °C, delay loop  $d_{in} = 2$  mm,  $L_t = 6$  m,  $F_{PPD} = 20$  mL/min,  $F_{TPC} = 20$  mL/min. The reaction was quenched at the outlet of the loop.

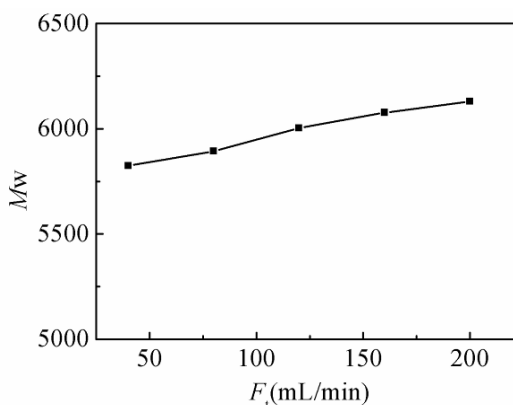
**Effects of temperature.** Besides the monomer molar ratio, the temperature also has an important influence on the polycondensation rate, as shown in Figure 6. Conducting the polycondensation process at a high temperature not only speeded up the reaction rate, but also weakened the adsorption interaction between HCl and PPD or acid amide groups, which makes pyridine less important. At the same time, it's easier and cheaper to get a high temperature than a low temperature which would reduce the energy cost. From these respects, operating the polycondensation in the microstructured chemical system at relatively high temperature is believed to have a potential application prospects.

**Effects of total flow rate.** The total flow rate in the microstructured chemical system could have influence on the mixing ability in the micromixer and further affect property of the product. Our previous work has shown that high mixing efficiency could be achieved in the micro-sieve mixer and the segregation indexes  $X_s$  were found in the range of  $10^{-2}$  to  $10^{-3}$ .<sup>28</sup> Effects of total flow rate ( $F_t$ ) on the average molecular weight of PPTA has been studied in our work, as shown in Figure 7. PPTA of higher average molecular weight was obtained when the total flow rate was higher, which could be contributed to better mixing ability in the micromixer when total flow rate increased. However, as a whole the product average molecular weight didn't change a lot when the total flow rate varied from 40 mL/min to 200 mL/min, which indicates that high enough mixing efficiency has been achieved when the total flow rate got above 40 mL/min. The average molecular weight is around 6000 and the product discharged the system before the system viscosity get too high. Flow resistance would increase rapidly if the polycondensation continues in the delay loop because the viscosity of reaction mixture increases with the polymer chain growth. So further reaction should be settled outside the delay loop if PPTA of

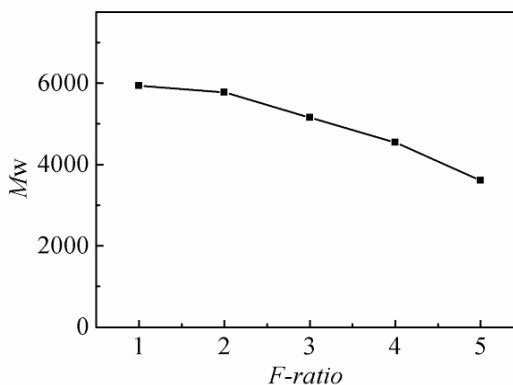
higher average molecular weight is wanted, and this part will be discussed later in this paper.

**Effects of flow rate ratio.** The work of Chen et al. has shown that changing the flow rate ratio of the two phases could adjust the mixing performance in a micro-sieve mixer.<sup>29</sup> The work of Wang et al. has further proven that the mixing performance in the micro-sieve mixer could have a significant effect on the result of a small molecule reaction process.<sup>30</sup> In the microstructured system, the flow rate ratio of PPD solution/TPC solution (*F-ratio*) directly influences the mixing performance of the reaction system, thus it is expected to further affect the whole PPTA synthetic process. Experiments were conducted varying the *F-ratio* to study its effect on the  $M_w$  of PPTA, which was realized by changing  $F_{TPC}$  and  $F_{PPD}$  while keeping  $F_t$  to be 120 mL/min. The experimental results are shown in Figure 8. From this figure, when the total flow rate is fixed, the optimum *F-ratio* is around 1. The average molecular weight of the product decreases with the increase of *F-ratio* which could result from less mixing efficiency in the micromixer when the *F-ratio* increases. Because the concentration of two monomers after mixing was kept unchanged, higher initial TPC solution concentration was needed when *F-ratio* increased. Larger concentration gradient needed higher mixing intensity, and less mixing efficiency was achieved when the mixing intensity was unchanged. As a result, PPTA with highest average molecular weight could be obtained when the flow rates of the two solutions were the same.

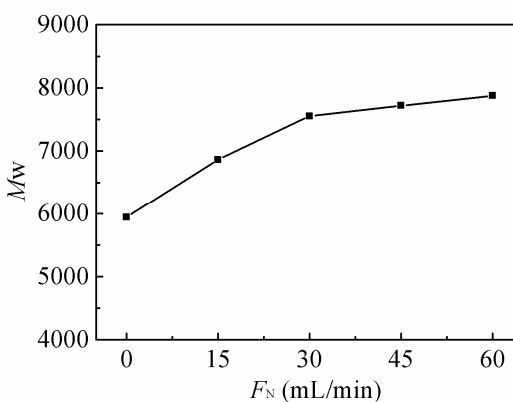
**Effects of gas agitation.** According to the work of Su et al. and Zhang et al., gas agitation could intensify the reaction in a small molecule reaction system.<sup>31, 32</sup> Thus we believe gas agitation may be a good choice to further enhance the mixing ability and promote the reaction in the PPTA synthesis process. In the experiments,  $N_2$  was added into the TPC solution at the entrance. Another important advantage of the introduction of gas phase is removing HCl from the reacting system to gas phase. Since the solubility of HCl in NMP-CaCl<sub>2</sub> solution is low and the interaction between HCl with PPD becomes weak at high temperature, the gas phase provides extra volatilization space in the confined reacting system, making the removal of HCl much easier. Effects of gas flow on the  $M_w$  of PPTA is shown in Figure 9. The  $M_w$  of PPTA showed an upward tendency with the increase of gas flow rate in the range of 0 ~ 60 mL/min, which implied that gas agitation did enhance the mixing ability in the polycondensation process. However, it is also noticed that the tilt of the curve got smaller which indicates gas agitation marginal effect got weaker when the gas flow rate got larger than 30 mL/min. Thus overall, the introduction of gas agitation to the micro system is beneficial to enhance the reaction efficiency and promote the  $M_w$  of the final polymer product, but the marginal effect of gas agitation gets smaller when the gas flow rate is larger than 30 mL/min.



**Fig. 7** Effect of total flow rate on the  $M_w$  of PPTA. Experimental conditions:  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 70$  °C, delay loop  $d_{in} = 3$  mm,  $L_t = 2.0 \sim 10.0$  m,  $F_{PPD} = 20 \sim 100$  mL/min,  $F_{TPC} = 20 \sim 100$  mL/min, residence time = 21.2 s. The reaction was quenched at the outlet of the loop.

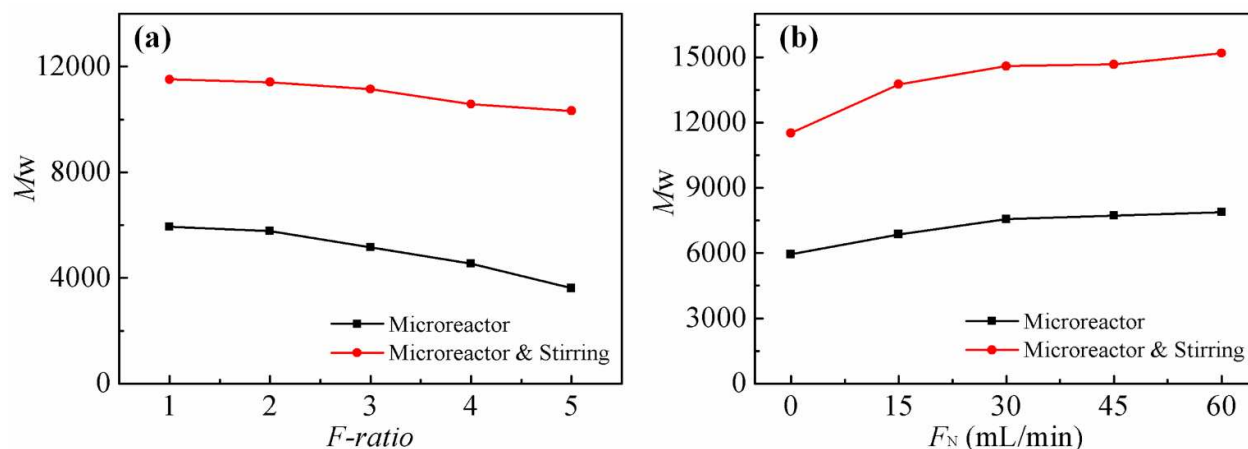


**Fig. 8** Effects of *F-ratio* on the  $M_w$  of PPTA. Experimental conditions:  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 70$  °C, delay loop  $d_{in} = 3$  mm,  $L_t = 6$  m,  $F_{PPD} = 60/80/90/96/100$  mL/min,  $F_{TPC} = 60/40/30/24/20$  mL/min,  $F_t = 120$  mL/min. The reaction was quenched at the outlet of the loop.



**Fig. 9** Effect of gas flow on the  $M_w$  of PPTA. Experimental conditions:  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 70$  °C, delay loop  $d_{in} = 3$  mm,  $L_t = 2.0 \sim 10.0$  m,  $F_{PPD} = 60$  mL/min,  $F_{TPC} = 60$  mL/min,  $F_N = 0 \sim 60$  mL/min, residence time = 21.2 s. The reaction was quenched at the outlet of the loop.





**Fig. 10**  $M_w$  of PPTA after the string reaction. Experimental conditions: (a)  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 70$  °C, delay loop  $d_{in} = 3$  mm,  $L_t = 6$  m,  $F_{PPD} = 60/80/90/96/100$  mL/min,  $F_{TPC} = 60/40/30/24/20$  mL/min,  $F_t = 120$  mL/min,  $r_s = 1500$  r/min,  $t_s = 30$  min; (b)  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 70$  °C, delay loop  $d_{in} = 3$  mm,  $L_t = 2.0 \sim 10.0$  m,  $F_{PPD} = 60$  mL/min,  $F_{TPC} = 60$  mL/min,  $F_N = 0 \sim 60$  mL/min, residence time = 21.2 s,  $r_s = 1500$  r/min,  $t_s = 30$  min.

#### Molecular weight of PPTA synthesized in the stirring tank

Since the viscosity of the reacting mixture increased sharply as the  $M_w$  of PPTA increases, the delay loop could not be extended infinitely considering the high flow resistance. To solve the problem, we developed a stirring tank at the outlet of the tube to further extend the reaction time. According to the above experimental result, the conversion of the reactive groups reached higher than 90% in the reaction loop, and then the reaction continued in the stirring tank. The experimental results after the stirring tank are given in Figure 10. Compared to that at the end of the loop, the  $M_w$  of PPTA was approximately doubled after the stirring reaction.

This two-step method combining a microreactor loop and a stirring tank is considered to be superior in several ways. First of all, more than 90% reaction has been finished in the continuous operated microreactor, which means that more than 90% of the reaction heat and by-product HCl are released in the microstructured system. So the temperature of the stirring reaction could be controlled well and the increase of the  $M_w$  of PPTA could be more easily. Secondly, since the  $M_w$  of PPTA is of several thousand at the end of the delay loop and the viscosity of the reacting mixture is not too high to be operated, the stirring tank can avoid the strong flow resistance and an efficient agitator is enough to mix the high viscous fluid, which simplified the tank design. Based on these considerations, this two-step method is believed to be suitable for this polymerization system, in which viscosity grows rapidly

with the increase of average molecular weight of polymer. Such a method is also expected to suit other polymerization systems that faced with the same problem.

#### Apparent kinetics of PPD/TPC polycondensation

To better understand this process, the apparent kinetics of polycondensation was studied and a kinetics model was built. The kinetics model of PPTA polycondensation in this work was based on that of Sunil et al. which had been successfully applied in the interfacial polycondensation field.<sup>33</sup> In this work, the model has been extended to a continuous flow process in a microstructured chemical system. The monomers and oligomers in the system are classified into three categories by different end groups: "A" for those having amine groups at both ends, "B" for those having acyl chloride groups at both ends and "C" for those having an amine group at one end and an acyl chloride group at the other end. "X" is used to represent for the repeat units. The subscripts represent the numbers of repeat units in the chain. Materials in the reaction system are listed in Table 2.

**TABLE 2** Reaction intermediates  $-(\text{CH}_2)_6-$  for benzene ring at para-positions)

Notation	Species	Structure
-X-	Repeat unit	$-\text{[NH}-(\text{CH}_2)_6\text{-NH-CO}-(\text{CH}_2)_6\text{-CO]}-$
$A_0$	PPD	$\text{NH}_2-(\text{CH}_2)_6\text{-NH}_2$
$B_0$	TPC	$\text{COCl}-(\text{CH}_2)_6\text{-COCl}$
$C_0$	Oligomer	$\text{NH}_2-(\text{CH}_2)_6\text{-NH-CO}-(\text{CH}_2)_6\text{-COCl}$
$A_n$	Oligomer	$\text{H-X}_n\text{-NH}-(\text{CH}_2)_6\text{-NH}_2$
$B_n$	Oligomer	$\text{COCl}-(\text{CH}_2)_6\text{-CO-X}_n\text{-Cl}$
$C_n$	Oligomer	$\text{H-X}_{n+1}\text{-Cl}$

**TABLE 3** Generalized reaction scheme for the formation of PPTA oligomers

Reaction	Values of m and n	Rate
$A_0 + B_0 \rightarrow C_0$	$m, n = 0$	$4kA_0B_0$
$A_m + B_n \rightarrow C_{m+n}$	$m, n \geq 0$	$4kA_mB_n$
$A_m + C_n \rightarrow A_{m+n+1}$	$m, n \geq 0$	$2kA_mC_n$
$B_m + C_n \rightarrow B_{m+n+1}$	$m, n \geq 0$	$2kB_mC_n$
$C_m + C_n \rightarrow C_{m+n+1}$	$m, n \geq 0$	$2kC_mC_n$

In the early stage of the polycondensation, viscosity of the reaction mixtures is not very high and the oligomers chain length is not so long, which assure the free movement of molecules in the system. So the equal reactivity hypothesis is used when building the kinetics model, as in Karode's work.<sup>34</sup> Because the solvent was kept unchanged (only NMP containing 6wt %  $\text{CaCl}_2$  was used), the rate constant between amine groups and acyl chloride groups is assumed to be "k". According to the work of Borkent et al., the reaction between amine groups and acyl chloride groups can be assumed to be a first order reaction.<sup>35</sup> The possible reactions among the oligomers and the reaction rates are shown in Table 3. Chains of all possible lengths need to be taken into consideration in theory. However, considering numerical computations closure, a maximum chain length  $n_{\text{max}}$  has been introduced. In the early stage of the polycondensation,  $M_w$  of PPTA prepared in the microstructured chemical system was several thousand, which corresponds to an average degree of polymerization of more than ten. So if the numerical value of  $n_{\text{max}}$  is set to be considerably larger than 10, it is reasonable. The concentration of polymers with chain length longer than  $n_{\text{max}}$  is considered to be zero. The net rate of generation of any species in the reaction system is given by the following expressions:<sup>33</sup>

$$r_{A_0} = -4kA_0 \sum_{n=0}^{n_{\text{max}}} B_n - 2kA_0 \sum_{n=0}^{n_{\text{max}}} C_n \quad (3)$$

$$r_{A_m} = 2k \sum_{n=0}^{m-1} A_{m-n-1} C_n - 4kA_m \sum_{n=0}^{n_{\text{max}}} B_n - 2kA_m \sum_{n=0}^{n_{\text{max}}} C_n, \quad m=1 \text{ to } n_{\text{max}} \quad (4)$$

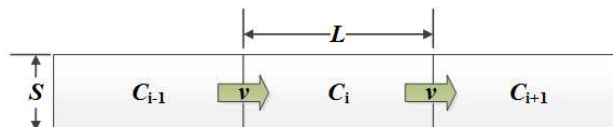
$$r_{B_0} = -4kB_0 \sum_{n=0}^{n_{\text{max}}} A_n - 2kB_0 \sum_{n=0}^{n_{\text{max}}} C_n \quad (5)$$

$$r_{B_m} = 2k \sum_{n=0}^{m-1} B_{m-n-1} C_n - 4kB_m \sum_{n=0}^{n_{\text{max}}} A_n - 2kB_m \sum_{n=0}^{n_{\text{max}}} C_n, \quad m=1 \text{ to } n_{\text{max}} \quad (6)$$

$$r_{C_0} = 4kA_0B_0 - 2kC_0 \sum_{n=0}^{n_{\text{max}}} A_n - 2kC_0 \sum_{n=0}^{n_{\text{max}}} B_n - 2kC_0 \sum_{n=0}^{n_{\text{max}}} C_n \quad (7)$$

$$r_{C_m} = 4k \sum_{n=0}^m A_{m-n-1} B_n + \sum_{n=0}^{m-1} k^* C_{m-n-1} C_n - 2kC_m \sum_{n=0}^{n_{\text{max}}} (A_n + B_n + C_n), \quad m=1 \text{ to } n_{\text{max}} \quad (8)$$

Note that in Equation (8):  $k^*=k$  if  $m-n-1 \neq n$ ;  $k^*=2k$  if  $m-n-1=n$ .

**FIG. 11** A PFR model for the flow process in the delay loop.

Since the flow velocity in the delay loops was fast and rapid mixing could be achieved in the micro-sieve mixer, the effect of axial mixing was ignored in this apparent kinetic study and the residence time was used to calculate the reaction time.<sup>36</sup> As shown in Figure 11, the delay loop is divided into  $N$  small segments and each segment is numbered sequentially. The length of each segment is  $L$ ; the cross sectional area of the delay loop is  $S$  and the average flow velocity is  $v$ .

$$\text{Accumulation} = \text{Input} - \text{Output} + \text{Generation} \quad (9)$$

Equation (9) is a balance equation suitable for all systems. For a certain composition in our system,  $C_i$  and  $r_i$  are used to represent the concentration and reaction rate in Number  $i$  segment. Then each item in Equation (9) is as follows:

$$\text{Accumulation} = 0 \quad (\text{Steady-state hypothesis}) \quad (10)$$

$$\text{Input} = (v * C_{i-1} + D \frac{C_{i-1} - C_i}{L}) * S \quad (11)$$

$$\text{Output} = (v * C_i + D \frac{C_i - C_{i+1}}{L}) * S \quad (12)$$

$$\text{Generation} = r_i * S * L \quad (13)$$

In the experimental process, the diffusion coefficient  $D \approx 10^{-8} \sim 10^{-12} \text{ m}^2/\text{s}$  in the solution,<sup>37</sup> the length of a segment  $L \approx 10^{-2} \text{ m}$  and the flow velocity  $v \approx 10^{-1} \text{ m/s}$ , resulting in  $\text{Pe} = vL/D \approx 10^5 \sim 10^9 \gg 1$ , so the diffusion term in Equation (11) and Equation (12) could be ignored. From Equation (9)-(13), the recurrence equation is as follows:

$$C_i = C_{i-1} + \frac{L}{v} r_i \quad (14)$$

For convenience,  $C_i$  and  $r_i$  are designed to be matrixes to represent all the species at the same time. The boundary conditions for the process is the given concentration of PPD ( $A_0$ ) and TPC ( $B_0$ ) at the entrance (the concentration of other species is 0). Reaction rates of all species in each segment could be calculated using Equations (3)-(8), and the concentration in the next segment could be got by Equation

(14). Step by step, the concentration of all species in the last segment could be got. The relationship between outlet  $M_w$  of PPTA and the concentration of each specie in the last segment is as follows:

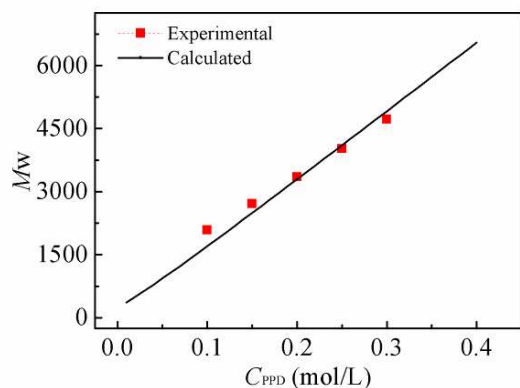
$$M_w = 238 \cdot \frac{\sum_{n=0}^{n_{\max}} n^2 \cdot (A_n + B_n + C_n)}{\sum_{n=0}^{n_{\max}} n \cdot (A_n + B_n + C_n)} \quad (15)$$

In this equation, "238" is the molecular weight of the repeat unit. Since the weight of the end groups is quite small compared to the numerous repeat units, only molecular weight of repeat units has been included in the equation for convenience.

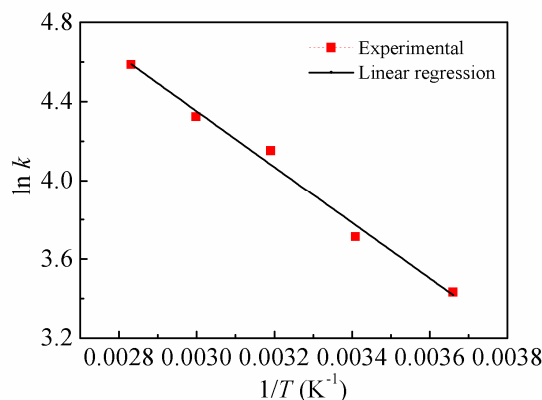
The  $M_w$  of PPTA varied when the monomer concentration changed, as shown in Figure 12. By using the above model, we got that the value of  $k$  was 24.9 L/(mol·s), and its confidence interval is between 22.6 L/(mol·s) to 27.1 L/(mol·s) at a confidence level of 95%. Figure 12 shows the calculated molecular weights fit well with the experimental data and we can see the monomer concentration has a significant effect on the polycondensation rate at the early stage of the reaction. In a very short time (less than 29 s), the  $M_w$  of PPTA increases fast. After the reaction rate constant  $k$  at 0 °C being obtained, its values at other temperature can also be got through the same way, thus the apparent activation energy ( $E$ ) as well as the pre-exponential factor ( $A$ ) can be calculated by using the Arrhenius equation, as following:

$$\ln k = -\frac{E}{RT} + \ln A \quad (16)$$

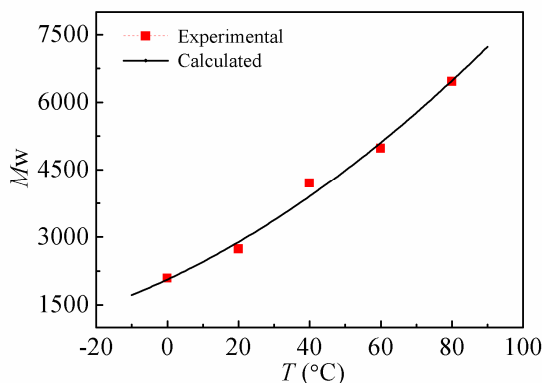
As shown in Figure 13 and Figure 14, the result of the least squares fitting shows that  $E = 12$  kJ/mol and  $A = 5.4 \times 10^3$  L/(mol·s). The confidence intervals for  $E$  and  $A$  are 9.5 ~ 14.0 kJ/mol and  $2.2 \times 10^3 \sim 1.3 \times 10^4$  L/(mol·s) at the confidence level of 95%, respectively. The value of  $E$  is slightly larger than that tested in a bath reactor (3.35 kJ/mol),<sup>13</sup> which could be due to more accurate temperature control in microstructured chemical system. Additional experiments also conducted to further verify the reliability of the kinetics model. As shown in Figure 15, the theoretical  $M_w$  of PPTA calculated by using the values of  $E$  and  $A$  mentioned above were basically in accordance with the experimental data too.



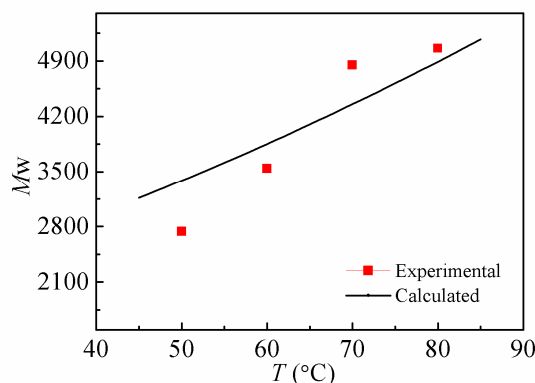
**Fig. 12** Effects of monomer concentration on the  $M_w$  of PPTA. Experimental conditions:  $C_{PPD} = 0.100 \sim 0.300$  mol/L,  $C_{TPC} = 0.102 \sim 0.306$  mol/L ( $aM$ -ratio = 1.02),  $T = 0$  °C, delay loop  $d_{in} = 2$  mm,  $L_t = 6$  m,  $F_{PPD} = 20$  mL/min,  $F_{TPC} = 20$  mL/min. The reaction was quenched at the outlet of the loop.



**Fig. 13** Linear regression between  $\ln k$  and  $1/T$ . The apparent activation energy and the pre-exponential factor can be calculated by the slope and the intercept.



**Fig. 14** Effect of temperature on  $M_w$  of PPTA. Experimental conditions:  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 0 \sim 80$  °C, delay loop  $d_{in} = 2$  mm,  $L_t = 6$  m,  $F_{PPD} = 20$  mL/min,  $F_{TPC} = 20$  mL/min. The reaction was quenched at the outlet of the loop.



**Fig. 15** Verification of the polycondensation kinetic model. Experimental conditions:  $C_{PPD} = 0.100$  mol/L,  $C_{TPC} = 0.102$  mol/L,  $T = 50 \sim 80$  °C, delay loop  $d_{in} = 3$  mm,  $L_t = 2$  m,  $F_{PPD} = 20$  mL/min,  $F_{TPC} = 20$  mL/min. The reaction was quenched at the outlet of the loop.

## Conclusions

A microstructured chemical system was designed elaborately to carry out the polycondensation of PPD and TPC for the preparation of PPTA. The product structure, property and composition were characterized by XRD, IR, POM, EA and SEM, proving that PPTA with high quality has been prepared. Effects of a number of factors, including apparent monomer molar ratio, temperature, total flow rate, flow rate ratio, gas agitation and monomer concentration on  $M_w$  of PPTA were investigated to determine the optimum conditions for the preparation of PPTA. The results showed that the change of total flow rate, flow rate ratio and gas agitation would enhance mixing in the microstructured system. A two-step method consisting of high reactive group conversion (more than 90%) in the microstructured chemical system and further increase of PPTA  $M_w$  in a stirring tank was developed, and the highest  $M_w$  reached 16,000. Conducting the polycondensation at high temperature made the process more convenient and environmentally friendly. The polycondensation kinetics has been studied and the results show that it's a first order reaction. By using the OLS method, we got the apparent activation energy  $E = 12$  kJ/mol and pre-exponential factor  $A = 5.4 \times 10^3$  L/(mol·s). This novel process ensures the polycondensation proceeding safely and conveniently. In our further work, more studies will be carried out to determine the distinct values of the reaction for better understanding the mechanism and to optimize the process for the preparation of higher  $M_w$  products.

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