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Non-aqueous Suspension Polycondensation in NMP-$CaCl_2$/Paraffin System − A New Approach for the Preparation of Poly(*p*-phenylene terephthalamide)*

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Abstract A non-aqueous suspension polycondensation method was proposed to proceed the reaction of *p*-phenylenediamine and terephthaloyl chloride for the preparation of poly(*p*-phenylene terephthalamide) (PPTA). The system was operated with NMP-$CaCl_2$ solution as the dispersed phase and inert liquid paraffin as the continuous phase. Each of NMP-$CaCl_2$ solution microdroplet suspended in paraffin served as a microreactor where the polycondensation took place. According to the results of TGA, XRD, IR, SEM and EA, PPTA with good quality was obtained through this novel method, and a number of main factors influencing this process were investigated to determine the optimum condition for the preparation of PPTA. Besides, this two-phase polycondensation system brings many unique advantages compared to the conventional solution polycondensation method, including a sealed reaction environment keeping the reactants away from oxygen and water, easy removal of HCl to promote the reaction, well-controlled temperature and low viscosity which means less energy cost.

Keywords: Poly(*p*-phenylene terephthalamide); Non-aqueous suspension polycondensation; Weight-average molecular weight; Microreactor; Microdroplets.

INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) is one of the most famous synthetic polymers in the world for its high performance properties in the aspects of tensile strength, roughness, corrosion resistance, weight and thermal stability[1−3]. The strength and modulus of PPTA are over 5 and 2 times than steel wire respectively, while its density is approximately only one fifth[4]. Such good properties make PPTA an excellent material in many industrial and civilian fields, such as asbestos replacement, ballistics, armor, marine laminates and so on[5−7].

As an important polymer product with growing demand, there are extensive researches ongoing for the PPTA synthesis in recent years[8−11]. The conventional technology to prepare PPTA is the low temperature solution polymerization method, which involves low initial reaction temperature and significant increase of viscosity as average molecular weight increases, leading to strict temperature control demand and high blending requirements[12]. Different from this common method, Morgan *et al*. reported an interfacial polycondensation process to prepare PPTA, in which the monomers terephthaloyl chloride (TPC) and *p*-phenylenediamine (PPD) were dissolved in an organic solvent (immiscible with water) and water, respectively, and PPTA was then synthesized at the phase interface where the two solutions contacted with each other[13]. The interfacial method

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for polycondensation process was investigated thoroughly in this case, including monomer concentration distribution in both solvents, removal of reaction heat, *etc*. To find other possible reactions to prepare PPTA, Yotsumoro *et al*. came up with a transesterification method. Polycondensation of aromatic diester and aromatic diamine was carried out in the presence of sulfobenzide, resulting in the synthesis of PPTA[14]. Hyunkook *et al*. from DuPont also mentioned a vapor-phase preparation of aromatic polyamides in a USA patent. Aromatic diacyl-chloride and aromatic diamine were evaporated to a mixture of gaseous tertiary amine and inert gas where they mixed and reacted. PPTA was obtained with HCl separated from the system[15]. From the above literatures, we can see new reactions or new reaction systems are still hot research points in developing new PPTA synthetic methods. However, considering the overall energy cost and controllability, the above methods raised by the researchers were not adopted widely in the industry, and the low temperature solution polycondensation is still most widely used in almost all commercial products, like Kevlar, Twaron, Technora *etc*[16]. This low temperature solution polycondensation method needs strict dehydration, deoxidation and accurate temperature control. And most importantly, it needs large energy input to mix the gelatinous or solid-state polymers.

To solve the above problems in the conventional low temperature solution polycondensation process to prepare PPTA, a new non-aqueous suspension polycondensation method is proposed in this article. In this new method, since each of the NMP-$CaCl_2$ solution microdroplet suspended in liquid paraffin serves as a microreactor separately[17, 18], the reactants are surrounded by non-reactive solvent, keeping them away from water and oxygen in the air, which is favorable for the polycondensation reactions[19]. With the reaction proceeding, HCl can diffuse from NMP-$CaCl_2$ solution microdroplets into liquid paraffin phase and be absorbed by pyridine molecules in the early stage of reaction process, which helps the polycondensation in NMP-$CaCl_2$ phase move forward[20]. In addition, since the reactants account for just a small part of the whole system, the system temperature won't change a lot due to the reaction heat and thus it can be controlled accurately during the process, and also, the system viscosity won't get too high even as the polymer molecular weight getting large, so it needs less energy to mix the reaction system. Based on the above considerations, a non-aqueous suspension polycondensation method is believed to be a promising solution to prepare PPTA controllably and economically. In such a process, the key point is to choose a suitable continuous phase, which should be inert for the reactions and have strong capacity in controlling temperature without thermal decomposition. Besides, the viscosity of the continuous phase should be neither too high nor too low, for the balance of energy cost and the stability of *N*-methyl-2-pyrrolidinone (NMP) microdroplets[21]. The addition of paraffin makes it easier to control temperature accurately, clean the reaction system and with no need of avoiding oxygen and water. All these aspects make the process more convenient.

In this paper, the novel non-aqueous suspension polycondensation approach is described detailedly to prepare PPTA using paraffin as the continuous phase. Since PPTA with higher average molecular weight has better mechanical properties and thermostability, the average molecular weight becomes the most important detection index for PPTA. The effects of different variables on the molecular weight of PPTA, such as phase ratio of NMP/paraffin, reaction time, stirring rate, *etc*. on the molecular weight of PPTA were studied in detail to determine the optimum operating condition for the preparation of PPTA.

EXPERIMENTAL

Materials and Equipments

P-phenylenediamine (PPD, > 99%), terephthaloyl chloride (TPC, > 99%), *N*-methyl-2-pyrrolidinone (NMP, 99%) were purchased from Acros Organics. The trace water in NMP was removed by adding NMP in molecular sieve and CaH_2 before the experiments. Paraffin liquid (chemically pure), $CaCl_2$ (> 96.0%), pyridine (99.5%) were bought from Beijing Modern Eastern Fine Chemical. $CaCl_2$ was heated for 4 h at 400 °C to dehydrate before use. Ethanol was from Beijing Chemical Works.

A high shearing emulsifying machine purchased from Fluko (Germany) was used to generate the suspension polycondensation system in a metal vessel. The temperature was controlled by a refrigerated

circulating bath, which was bought from Shanghai Fangrui Instrument Company. A Ubbelohde viscometer with capillary diameter 0.9–1.0 mm was used to measure the weight-average molecular weight of PPTA at 30 °C.

Operation and Reaction Process

In each experiment, 100 mL dried NMP was first added into the metal vessel, which had been purged by nitrogen to remove oxygen. Then the emulsifying machine was turned on and $CaCl_2$ was added into NMP. After about 20 min, all $CaCl_2$ was dissolved. PPD and 6 mL pyridine were then added into NMP, which dissolved in less than 1 min. After that the NMP solution was dispersed in 100 mL liquid paraffin immediately under the strong shearing force from the emulsifying machine, forming a non-aqueous suspension with droplet size in dozens of micrometers, as shown in Fig. 1. Then TPC was added in and the reaction started. In the whole process, the vessel temperature was controlled at a certain temperature. After a period of time, the reaction was quenched by washing the reaction system with amount of deionized water. Then the polymer was immersed in ethanol for 8 h to remove water and NMP absorbed in PPTA further. Finally, the prepared PPTA was dried at 120 °C for 12 h before being tested.

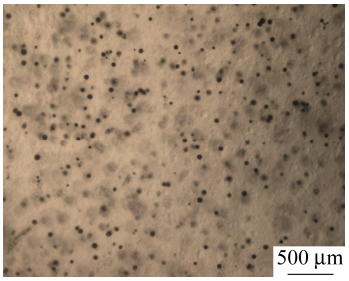

Fig. 1 NMP-$CaCl_2$ solution microdroplets suspended in liquid paraffin under microscope
The average size of droplets is dozens of micrometers.
Conditions: phase ratio of NMP/paraffin 100/100 and stirring rate 10000 r/min.

The polycondensation reaction between PPD and TPC is shown in Fig. 2. At the beginning of the reaction process, PPD was dissolved in NMP-$CaCl_2$ solution microdroplets while TPC in liquid paraffin phase. Because both PPD and TPC molecules prefer to dissolve in NMP-$CaCl_2$ phase, TPC molecules transported from liquid paraffin into NMP-$CaCl_2$ microdroplets as soon as the two phases got contact, after which the reaction began. Due to the interaction between TPC and pyridine, TPC was stabilized and free acyl chloride groups concentration available in the microdroplets decreased, contributing to slower initial reaction rate which made the process more controllable and the products more uniform. As shown in Fig. 2, HCl was generated as a by-product. If an amount of HCl molecules remained in NMP-$CaCl_2$ microdroplets, they could react with the existing oligomers which meant the reaction proceeded in the reverse direction, or they could react with the amino groups that prevented the further growth of the polymer chain. To avoid these two defective side reactions, we used pyridine, which was added into paraffin phase directly at the beginning of experiment, to remove HCl from the NMP-$CaCl_2$ microdroplets in the early stage of the reaction process. The decrease of HCl then contributed to the polycondensation process moving forward. As the reaction continued, the pyridine-HCl salts kept a balance between the two phases. Since the HCl molecules had been absorbed by the pyridine, they would not destroy the polycondensation.

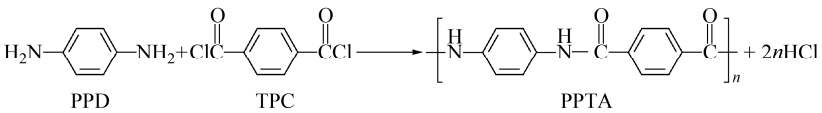

Fig. 2 Polycondensation equation between PPD and TPC to synthesize PPTA

To obtain PPTA with high molecular weight, it is important to mix the reaction mixtures thoroughly. In the experiment, NMP-$CaCl_2$ microdroplets were mixed under stirring effects of the high shearing emulsifying machine. NMP-$CaCl_2$ microdroplets were stretched or extruded in the high-speed rotating paraffin environment quickly. At the same time, violent internal circulation phenomena took place in the microdroplets because of the frictional force between NMP-$CaCl_2$ microdroplets and paraffin. All these effects helped mix the reactants and benefited further increase of PPTA M_w.

The schematic diagram for the whole non-aqueous suspension polycondensation process is shown in Fig. 3.

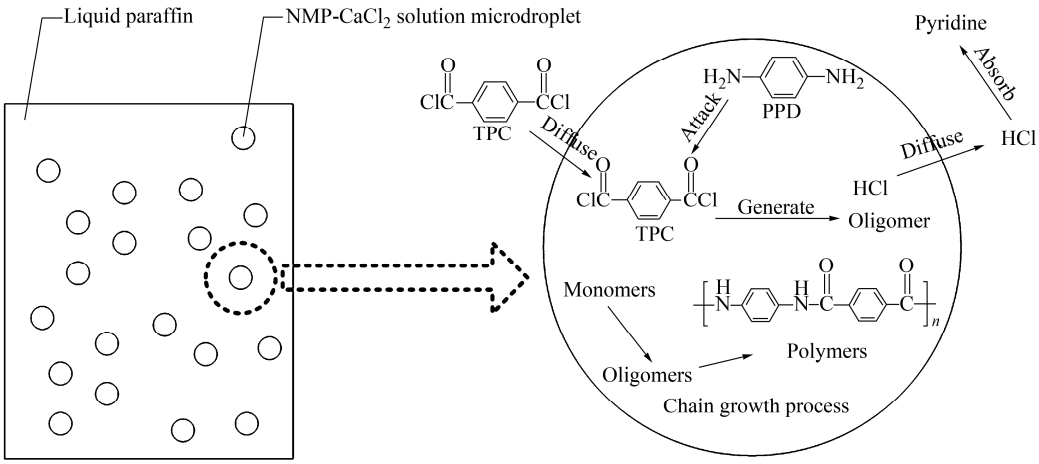

Fig. 3 Schematic diagram of the non-aqueous suspension polycondensation process

Characterization of PPTA

Thermal gravimetric analysis (TGA), X-ray diffraction (XRD), infrared (IR) spectroscopy, scanning electron microscopy (SEM) and elemental analysis (EA) were applied to characterize the product PPTA. TGA was operated from 30 °C to 900 °C at a heating rate of 20 K/min, using a simultaneous thermal analyzer (STA 409 PC, Netzsch Instruments, Inc., Germany). The crystal form of the polymer was characterized by XRD (max-RB, Rigaku Corporation D, Japan). The molecular structure of PPTA was measured by IR spectrum, using a Fourier transform infrared spectrometer (TENSOR 27, Bruker Optics Instruments Company Germany). Detailed structures were observed using SEM (JSM-7401, JEOL Ltd, Japan). Nitrogen, carbon, hydrogen and oxygen element contents of PPTA were measured with an elemental analyzer (VARIO EL III, Elemental Analysis Systems Company, Germany).

The molecular weight was measured by inherent viscosity method. Inherent viscosity is defined as follows:

$$\eta_{\text{inh}} = \ln(\frac{t_1}{t_2}) / c \tag{1}$$

where η_{inh} is the inherent viscosity; t_1 and t_2 are the solution flow time and the solvent flow time in the viscometer, respectively; c is the solution concentration.

Normally the solution concentration is 0.5 g/dL (5 kg/m^3) for the testing and calculation of PPTA. In the experimental test, sulfuric acid is used as the solvent. The relationship between weight-average molecular weight and inherent viscosity of PPTA solution is

$$M_{\text{w}} = 3902.39\eta_{\text{inh}}^{1.556} \tag{2}$$

which is used to calculate the M_w of PPTA in this paper[22].

RESULTS AND DISCUSSION

Structure and Composition Characterization of the Prepared PPTA

The typical TGA results of the experimental product are shown in Fig. 4(a) and 4(d), indicating the polymer starts to decompose at 550 °C. This thermal decomposition temperature coincides with the value in literature[23].

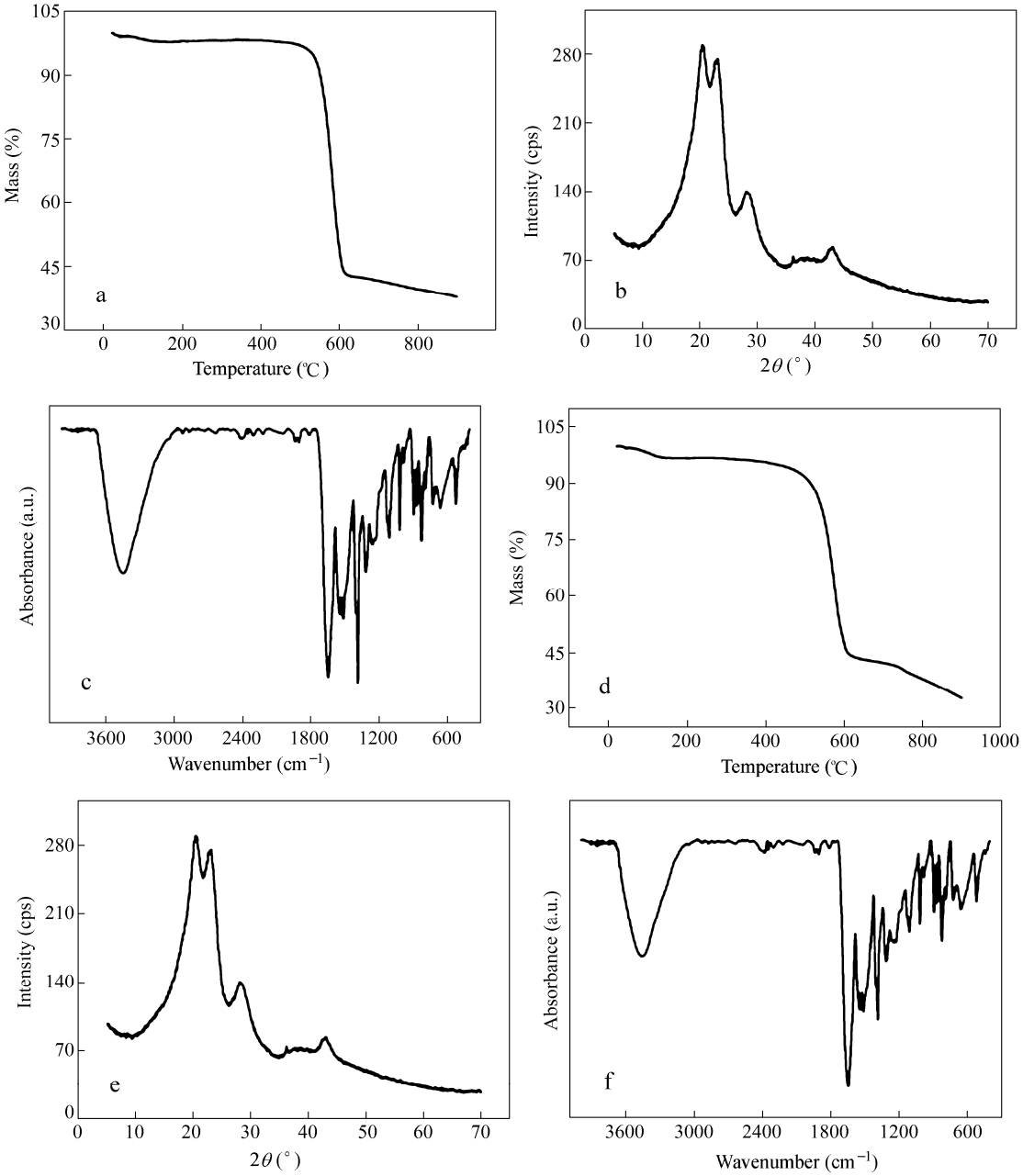

Fig. 4 Structure and composition characterization of a PPTA sample: (a, d) TGA curves; (b, e) XRD curves; (c, f) IR spectrum curves

Conditions for (a–c): phase ratio of NMP/paraffin 100/100, reaction time 30 min, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L, monomer molar ratio 1.00 and temperature 0 °C. Conditions for (d–f): phase ratio of NMP/paraffin 100/100, reaction time 30 min, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L, monomer molar ratio 1.02 and temperature 0 °C.

Figures 4(b) and 4(e) show the XRD results of samples prepared under different conditions. 20.5°, 23.0° and 29.0° are diffraction peaks of 110, 200, 004 crystal faces in PPTA, which are also consistent with previous literature[24]. The IR results are shown in Figs. 4(c) and 4(f). The absorption band at 1640 cm^{-1} is strong and it is caused by the stretching vibration of C=O, which is called the amide I band. Absorption bands at 1540 cm^{-1} and 1260 cm^{-1} are caused by the deformation coupling vibrations of O=C−N and N−H, and they are called the amide II band and amide III band, respectively. The IR spectrum result is also consistent with what has been reported in literature[25]. The SEM pictures of the prepared samples are shown in Fig. 5. The particle size is around dozens of micrometers. There are a lot of stripes on the surface caused by the rigid and rod-like macromolecules of PPTA[26].

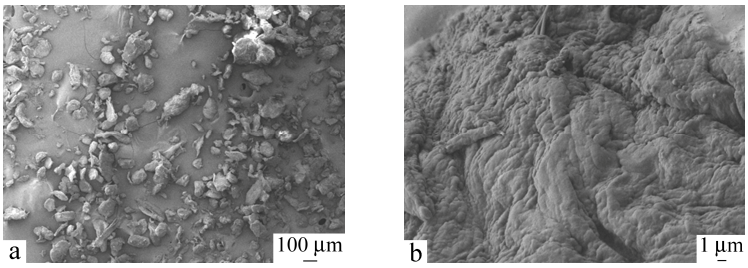

Fig. 5 SEM pictures of a PPTA sample. (a) overall picture of a number of particles; (b) surface morphology of a single particle
Preparation conditions: phase ratio of NMP/paraffin 100/100, reaction time 30 min, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L, monomer molar ratio 1.00, and temperature 0 °C.

Table 1 shows the EA results of three PPTA samples. The amounts of N, C, H and O are roughly consistent with the theoretical values. The tiny difference of elements content between measuring result and theoretical value is possibly caused by the moisture in PPTA samples, which explains the increase of H and O contents but quite small difference of C/N values.

Table 1. EA results of the prepared PPTA

Sample No.	N	C	H	O	C/N
Theoretical value	11.76	70.59	4.20	13.45	6.00
1	11.32	68.92	4.28	15.48	6.09
2	11.40	69.23	4.26	15.11	6.07
3	11.41	69.14	4.27	15.18	6.06

The structure and composition results confirm that the polymer prepared *via* the method of non-aqueous suspension polycondensation is PPTA indeed, and it is further validated by the facts that each performance testing consists with literature values or theoretical values very well.

Effects of Different Variables on the M_w of PPTA

As mentioned above, PPTA with higher average molecular weight has better mechanical properties and thermo stability. That is to say, the average molecular weight mainly decides the PPTA product properties, and PPTA with different average molecular weight has different application fields, so it becomes the most important detection index for PPTA. In the paper, we have investigated effects of a number of variables on the weight-average molecular weight (M_w) of PPTA, in hope to adjust the M_w of PPTA by changing these factors in the preparation process depending on the potential application. We have also found the optimum operating condition for the preparation of PPTA, under which the highest M_w reaches approximately 18000.

Phase ratio of NMP/paraffin

The effect of phase ratio of NMP/paraffin has been studied by changing the amount of NMP in each experiment from 10 mL to 100 mL with liquid paraffin consistent to be 100 mL, and the result is shown in Fig. 6. As can be

seen, with the concentration of both monomers unchanged, the amount of monomers is proportional to the volume of NMP phase. When the amount of NMP phase is small, the amount of monomers is small, too. Under such condition, a little TPC left in paraffin liquid, a small error in weighting or a small amount of side reactions would have a large impact on the molar ratio of monomers. When there is substantial excess of one kind of monomer, the redundant monomer would stay at both ends of every chain, which prevents the chain growth. 1% difference of monomer molar ratio can make the weight-average molecular weight change 50%, as shown in Fig. 11. As a result, when the amount of NMP phase is very small, a serious unbalance of monomer molar ratio causes molecular weight of PPTA quite small. On the other hand, if the amount of NMP phase is too large, NMP microdroplets would coalescences easily which may destroy the stability of the reaction system. In the experiments, when the phase ratio of NMP/paraffin exceeded 1.1, the NMP microdroplets coalescence quickly. Taken together, an appropriate choice is that the volume ratio of NMP and paraffin liquid gets value of 1.

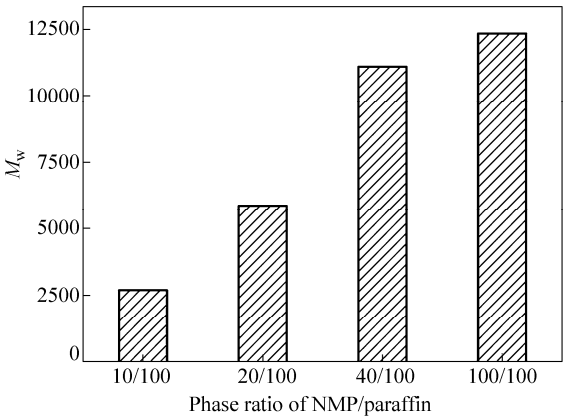

Fig. 6 Effects of phase ratio of NMP/paraffin on the M_w of PPTA
Conditions: reaction time 30 min, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L, monomer molar ratio 1.00 and temperature 0 °C.

Reaction time

Figure 7 presents the effect of reaction time on the M_w of PPTA. The reaction of PPD and TPC is an ultra-fast reaction, and the weight-average molecular weight of PPTA grows to as high as 9000 in less than 5 min during the experiments. Then the molecular weight increases slowly until it gets close to a limit value, showing the molecule growth almost stopped. At the beginning of the reaction, there are abundant acyl chloride groups and amino groups, and the viscosity of NMP-$CaCl_2$ solution is low enough to allow the monomers and oligomers to move around easily, so the probability of collisions between these reactant groups is high. As a result, the reaction rate is fast. In contrast, after the average molecular weight is up to about 10000, the concentration of left acyl chloride groups and amino groups is quite low compared to the initial concentration. Moreover, the viscosity of the NMP-$CaCl_2$ phase becomes very high and NMP-$CaCl_2$ microdroplets even turn into jelly or solid, making it difficult for oligomers to transfer, which is bad for further chain growth. What is worse, some of the reactive groups might be embedded in the macromolecules and can't get in touch with others. All these reasons result in the reaction rate decreasing quickly and the molecular weight tends to be relatively stable after 30 min. Therefore, 30 min may be a good choice for the reaction time.

Stirring rate

Stability of suspension polymerization process and properties of products are related to the stirring rate. Arshady *et al*. found that the average droplet size in suspension process is roughly inversely proportional to the stirring rate or power for mixing[27], as shown in Eq. (3).

$$\overline{d} = k\frac{D_V \cdot R \cdot v_d \cdot \varepsilon}{D_S \cdot N \cdot v_m \cdot C_s} \tag{3}$$

where $\overline{d}$ is average particle size; k is parameters such as apparatus design, self-stabilization, type of stirrer, *etc.*; D_V is the diameter of vessel; D_S is the diameter of stirrer; R is the volume ratio of the droplet phase to suspension medium; N is the stirring rate (or power of mixing); v_d is the viscosity of the droplet phase; v_m is the viscosity of the suspension medium; ε is the interfacial tension between the two immiscible phases; and C_S is the stabilizer concentration.

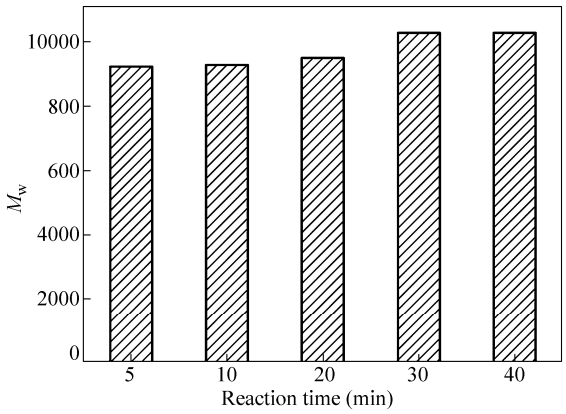

Fig. 7 Effects of reaction time on the M_w of PPTA
Conditions: phase ratio of NMP/paraffin 100/100, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L, monomer molar ratio 1.00 and temperature 0 °C.

PPTA has a rigid chain, resulting in the microstructure rod-like. So as the stirring rate increases, the microdroplets size decreases which is disadvantageous for the movement of macromolecules. Therefore, increase of stirring rate is unfavorable for growth of molecular weight from this perspective. On the other hand, the increase of stirring rate means more energy imported into the system, and the mixing is enhanced. When the viscosity of the NMP-$CaCl_2$ solution phase gets high, more powerful mixing ability contributes to a fiercer internal flow in NMP-$CaCl_2$ microdroplets, which results in larger collision possibility between different groups. As a result, increase of stirring rate is beneficial for growth of molecular weight from this perspective. In conclusion, increase of stirring rate has opposite effects on the molecular weight of PPTA when analyzing from different perspectives. In experiments, the actual effect depends on which perspective is dominant. Figure 8 shows that when the stirring rate increases, the weight-average molecular weight of PPTA rises in the first stage and then decreases, but the overall change is not significant.

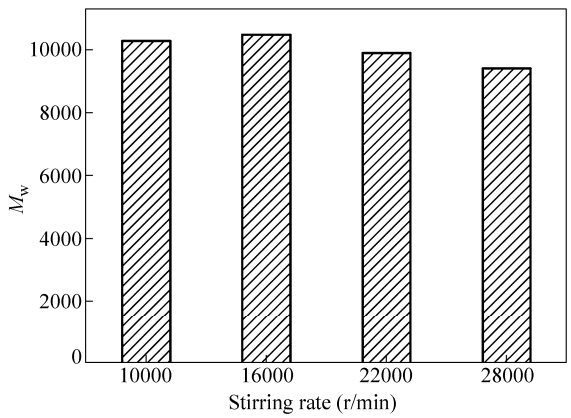

Fig. 8 Effects of stirring rate on the M_w of PPTA
Conditions: phase ratio of NMP/paraffin 100/100, reaction time 30 min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L, monomer molar ratio 1.00 and temperature 0 °C.

$CaCl_2$ concentration

$CaCl_2$ is a good hydrotropy agent because of its good effects in increasing PPTA solubility in NMP and its low price. Effect of $CaCl_2$ concentration has been studied, as shown in Fig. 9. When there is no $CaCl_2$, strong hydrogen-bond interaction between macromolecules makes PPTA chains get together and causes them to precipitate easily. Under the presence of $CaCl_2$, the complexation between calcium ions and carbonyl groups contributes to destroying the strong hydrogen bonding. Less aggregation contributes to higher solubility of PPTA in NMP-$CaCl_2$ solution, as shown in Fig. 10. Generally, $CaCl_2$ concentration has a significant impact on the molecular weight of PPTA. When the $CaCl_2$ concentration increases from 4 wt% to 10 wt%, the weight-average molecular weight increases 50% approximately. However, it should also be mentioned that since $CaCl_2$ has to be washed away form the final PPTA product later, more $CaCl_2$ means that more water is needed to wash them away.

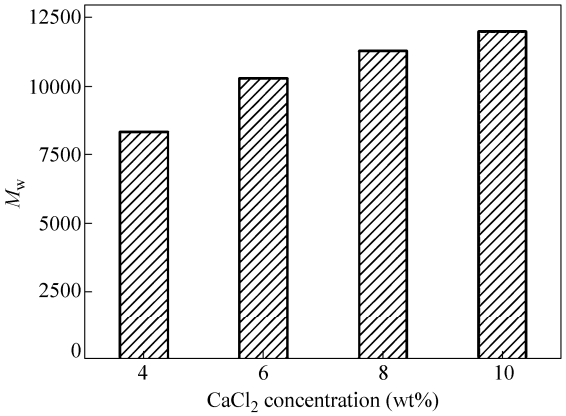

Fig. 9 Effects of $CaCl_2$ concentration on the M_w of PPTA
Conditions: phase ratio of NMP/paraffin 100/100, reaction time 30 min, stirring rate 10000 r/min, monomer concentration 0.4 mol/L, monomer molar ratio 1.00 and temperature 0 °C.

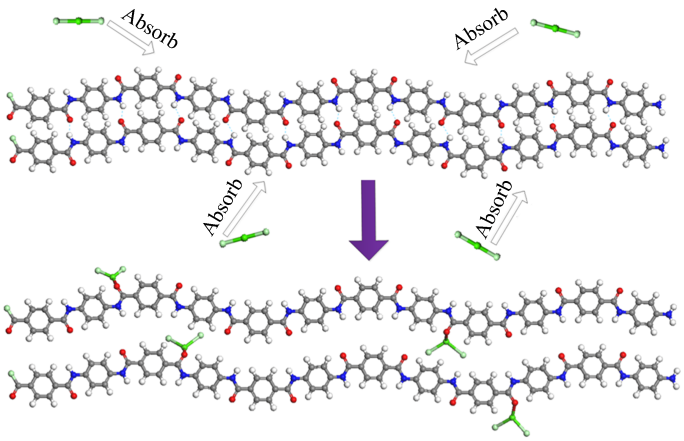

Fig. 10 Schematic diagram showing the adsorption of $CaCl_2$ on PPTA macromolecules and destroying the strong hydrogen bonding among them
In the diagram, gray balls represent for carbon atoms, white for hydrogen, red for oxygen, blue for nitrogen, green for calcium and light green for chloride. Light blue dash lines between oxygen atoms and hydrogen atoms represent for hydrogen bonds.

Monomer concentration

Figure 11 shows the effect of monomer concentration on the M_w of PPTA. As can be seen, the monomer concentration has a large effect on the molecular weight. A range of 0.3 mol/L to 0.4 mol/L of the monomer

concentration is a good choice for the preparation of PPTA with higher molecular weight. When the concentration is low, the side reactions caused by impurities, like oxidation of PPD with trace oxygen and hydrolysis of TPC with trace water, would impede the growth of average molecular weight. When the concentration is too high, large concentration gradient makes it difficult for TPC to transport from liquid paraffin into NMP-$CaCl_2$ microdroplets uniformly, which would result in a few macromolecules formed at the first stage, causing the reactive groups embed in them, which is unfavorable for further polymer chain growth. When the concentration is proper, the monomer molar ratio is better controlled and there is appropriate collision probability between monomers, oligomers and polymers, which both do favor to higher molecular weight. Therefore, a medium monomer concentration range (0.3 mol/L to 0.4 mol/L) is a good choice for the preparation of PPTA with high molecular weight.

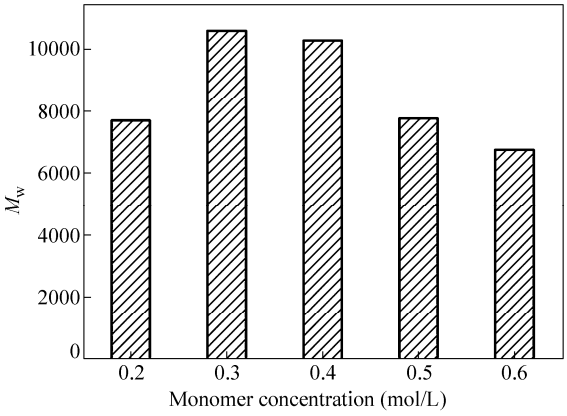

Fig. 11 Effects of monomer concentration on the M_w of PPTA
Conditions: phase ratio of NMP/paraffin 100/100, reaction time 30 min, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer molar ratio 1.00 and temperature 0 °C.

Monomer molar ratio

The effect of monomer molar ratio on the weight-average molecular weight of PPTA is presented in Fig. 12. The figure shows that PPTA with higher molecular weight can be prepared when the molar ratio of TPC: PPD is about 1.02. In theory, the highest molecular weight PPTA can only be synthesized when the molar ratio is exactly equal to 1, as shown in Eq. (4)[28]. However, in practical experiments, the monomers aren't of 100% purity and mole number errors can't be avoided in the weighing process. Moreover, TPC needs to diffuse from

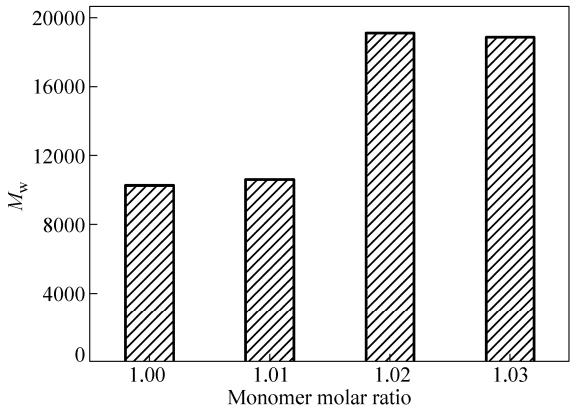

Fig. 12 Effects of monomer molar ratio on the M_w of PPTA
Conditions: phase ratio of NMP/paraffin 100/100, reaction time 30 min, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L and temperature 0 °C.

liquid paraffin to NMP-$CaCl_2$ microdroplets in the preparation process, so small amount of TPC would be left in the paraffin phase inevitably. As a result, a little more quantity of TPC than PPD is needed in the process for high molecular weight PPTA.

Theoretical equation for the calculation of degree of polymerization is as follows:

$$\overline{X}_n = \frac{1+r}{1+r-2rP} \tag{4}$$

in which, $\overline{X}_n$ is degree of polymerization; r is the molar ratio of two monomers, and the range of r is 0-1; P is the extent of functional groups reacted, and the range of P is 0-1.

Temperature

Figure 13 presents the effect of temperature on the M_w of PPTA. The molecular weight increases as the temperature rises. In contrast, Ji *et al*. found that the M_w decreased when the temperature rised in the range from 0 °C to 15 °C using low temperature solution polycondensation method[29]. In that method, qualities of PPD and TPC undergo deterioration quickly when temperature is high. Part of reactive groups on monomer molecules could lose efficacy and 'monomers' with single reactive group which are perfect chain terminators generate, resulting in low molecular weight product. However, in the non-aqueous suspension polycondensation method, PPD is dissolved in NMP-$CaCl_2$ microdroplets which are surrounded by liquid paraffin during the process. A little rise of temperature won't speed up the deterioration of PPD and TPC dramatically because of lack of oxygen and water. On the contrary, rise of temperature increases the solubility of monomers, oligomers and polymers. Besides, it decreases the viscosity of the NMP-$CaCl_2$ microdroplets which makes the reactants move more actively. From these two perspectives, molecular weight increases with the rise of temperature，consistent with the experimental result. Such results also verify the superior aspect of this non-aqueous suspension polycondensation method that we could increase the molecular weight of the product by raising temperature properly without worrying the metamorphism of PPD and TPC, as in the case of low temperature solution polycondensation method.

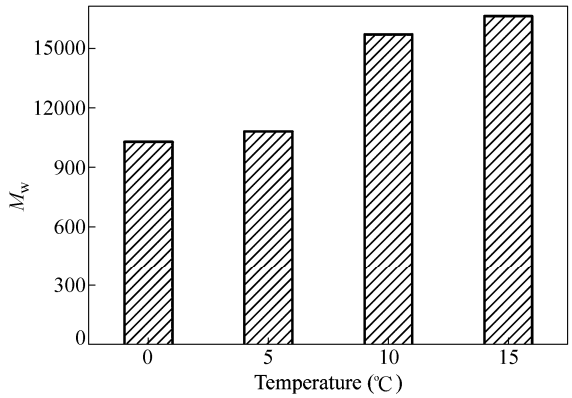

Fig. 13 Effects of temperature on the M_w of PPTA
Conditions: phase ratio of NMP/paraffin 100/100, reaction time 30 min, stirring rate 10000 r/min, $CaCl_2$ concentration 6 wt%, monomer concentration 0.4 mol/L and monomer molar ratio 1.00.

CONCLUSIONS

In this paper, the polycondensation reaction between *p*-phenylenediamine (PPD) and terephthaloyl chloride (TPC) was tested in a non-aqueous suspension system to synthesize poly(*p*-phenylene terephthalamide) (PPTA). Each of the NMP-$CaCl_2$ solution microdroplets suspended in paraffin liquid serves as a microreactor in which the polycondensation takes places. Application of this new approach leads to less strict demand for dehydration and deoxidation of working system, easy removal of HCl making reaction move forward, well-controlled temperature and low system viscosity with less energy cost. The molecular weight can be adjusted easily by

changing the following reaction parameters: phase ratio of NMP/paraffin, reaction time, stirring speed, $CaCl_2$ concentration, monomer concentration, monomer molar ratio and temperature. PPTA with the highest weight-average molecular weight of 18000 was obtained with this method in the experiments steadily and repeatably. Furthermore, we are currently studying the kinetics of polycondensation and the role of $CaCl_2$ in the process experimentally and theoretically, hoping to improve the M_w of PPTA further. We will also proceed the polycondensation in microchannel reactors, in which microdroplets can form more controllably[30], and the temperature is more precise[31] which makes the process more steady and safer[32]. PPTA of higher M_w is also expected to be prepared using other new emerging technology.

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