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# Accelerating the “one-pot” melt polycondensation for thermotropic liquid crystalline polymers by introducing a second acetylating agent

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Thermotropic liquid crystalline polymers (TLCPs) have been widely studied since the 1970s, and producing TLCPs in a more efficient way for both cost saving and performance enhancement has always intrigued us. One of the most effective ways is further increasing the degree of acetylation of monomers. Herein, we report a strategy of introducing a second acetylating agent, acetylates of polyphenols, which works at high temperatures when the first acetylating agent, acetic anhydride, is removed from the system. A model reaction proved that benzene-1,3,5-triyl triacetate (PGAc) could efficiently acetylate phenol to form phenyl acetate at 200 °C in a short time (1 h), which was evidenced by <sup>1</sup>H NMR. Adding the second acetylating agent, PGAc, in the polycondensation of HBA and HNA without modifying the process flow accelerated the propagation stage even in the absence of catalyst as shown by the data of distillate with time and the evacuation time of the melt polycondensation. Furthermore, other acetylates of polyphenols were also found to be acetylating agents to accelerate the polymerization and form a series of new TLCPs, inserting a small amount of which didn't affect the chemical structures and thermodynamic properties much. The strategy of introducing a second acetylating agent shows great potential in both theoretical research and practical application.

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## 1. Introduction

Thermotropic liquid crystalline polymers (TLCPs), as a widely studied special engineering plastics, are well known for their excellent overall performance, including high heat resistance, low water absorption, high strength, high modulus, small coefficient of thermal expansion, and dielectric performance,<sup>1,2</sup> and have received much attention from scientists and engineers worldwide since their invention in the 1970s.<sup>3,4</sup> TLCPs favor the formation of a liquid crystalline phase with excellent flow ability at temperatures higher than their melting point and can be used to form 1D fibers, 2D films *via* extrusion molding, and complicated 3D items by injection molding, which has been widely applied in aerospace, for special protection, electronics and electrical appliances.<sup>5–8</sup>

TLCPs are usually polymerized from aromatic monomers with phenolic hydroxyl and carboxyl groups with the help of a catalyst, *e.g.* organic base, acetate, or metallic oxide.<sup>9–11</sup> For example, Vectra-type TLCPs, developed by Celanese Corp. in the U.S., are made of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA).<sup>2</sup> Traditionally, the phenolic hydroxyl in HBA or HNA is less active in esterification reactions due to the electron-withdrawing effect of the aromatic rings, and the direct esterification of the phenolic hydroxyl is much more difficult

and prior acetylation is necessary.<sup>4,12</sup> Acetic anhydride is a widely used agent to convert the phenolic hydroxyl into a highly active acetoxy group, but acetic anhydride and its derivative acetic acid are both easily removed with the gradual increase in the reaction temperature, meaning a high degree of acetylation cannot occur, *e.g.* near to 100%.<sup>18</sup> Besides, some acetylates of the monomers or oligomers will lose their acetoxy group causing mechanism transition from acidolysis to phenolysis, which further lowers the ratio of acetoxy in the melt polycondensation at high temperature.<sup>13</sup> A lower degree of acetylation is not conducive to push the melt polycondensation and solid-state polycondensation forward, since the resulting TLCPs propagate slowly for the reason that phenolysis proceeds much slower than acidolysis.<sup>14</sup> For enhancing the degree of acetylation, a two-step strategy has been used, where acetylates of monomers were purified in water first and then mixed to polymerize, but with lower total efficiency and higher cost.<sup>11</sup> Catalysts with high efficiency have been reported, including a catalytic composite made of cobalt(III) acetylacetonate and zinc acetate, and an organic base with higher boiling point,<sup>15,16</sup> but which also leaves catalyst in the TLCPs and possibly causes side reactions during processing and the later application.

Herein, a novel strategy involving the introduction of a second acetylating agent, an acetylate of a polyphenol, was developed. The acetate of phloroglucinol (PGAc) was founded to be an acetylating agent to efficiently acetylate phenol to form phenyl acetate, which was indicated by <sup>1</sup>H NMR study. In the

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polycondensation of HBA and HNA, acetic anhydride and PGAc, as the first and second acetylating agent, respectively, could obviously accelerate acidolysis to quickly form TLCPs even in the absence of catalyst. Furthermore, other acetylates of polyphenols were also found to act as the second acetylating agents in the “one-pot” melt polycondensation of HBA and HNA, where a series of new TLCPs were obtained. These TLCPs showed almost the same chemical structures and thermodynamic properties, which suggested that adding a second acetylating agent had no obvious impact on the performance of the TLCPs. The novel strategy of introducing a second acetylating agent is very promising both in theoretical research and practical application.

## 2. Experimental

### 2.1. Materials

Acetic anhydride (AA), imidazole (IMD), zinc acetate ( $\text{Zn}(\text{OAc})_2$ ), (1,1'-biphenyl)-4,4'-diol (BP), hydroquinone (HQ), phenol (PO), phloroglucinol (PG), resorcinol (RC), and 1,3,5-benzenetricarboxylic acid (BA) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All of them were used directly without further purification.

### 2.2. Model reaction

To test the effect of PGAc on the acetylation of the phenolic hydroxyl, a model reaction was designed and carried out. PO was chosen to act as the model compound for the monomer and was mixed with PGAc in a molar ratio of 22/3 at room temperature. The reaction was kept at 200 °C for 1 h, and the mixture without further purification was sampled to test using  $^1\text{H}$  NMR.

### 2.3. Acetylation reaction of polyphenols

The synthesis processes of all acetylates were similar. Taking the synthesis of PGAc as an example, PG (12.61 g, 0.1 mol), AA (40.84 g, 0.4 mol), and  $\text{Zn}(\text{OAc})_2$  (18.35 mg, 0.1 mmol) were added into a 250 mL three-necked round-bottom flask, and the system was slowly purged with nitrogen for 2 min to remove air. The flask was placed in an oil bath, and the temperature was slowly raised to 140 °C and maintained there for 2 h. After the reaction was completed, the solution was slowly dropped into a beaker containing deionized water, and stirred at r.t. for 1 h. The precipitate was washed with water three times and dried overnight at 120 °C. 24.05 g of white powder, PGAc, was obtained in a yield of 95.44%.

Other acetylates were prepared in a similar way, and the corresponding compounds were named as BPAC, HQAc, POAc, RCAC from BP, HQ, PO, PG and RC, respectively.

### 2.4. “One-pot” melt polycondensation

Taking the preparation of PGAc-TLCP-2 as an example, HBA (22.08 g, 0.16 mol), HNA (11.07 g, 0.059 mol), PGAc (0.17 g, 0.67 mmol), and AA (24.56 g, 0.24 mol) were added in a flask. The system was slowly purged with nitrogen for 10 min to remove air, and acetylation was carried out at 140 °C for 2 h to convert the phenolic hydroxyl into an acetoxy group. The temperature

was slowly raised to 300 °C over 3 h, and vacuum pumping was applied when the temperature was stable to start the last stage of polymerization. PGAc-TLCP-2 was obtained in this way.

Other TLCPs were prepared by only changing the additive or catalyst and without any modification of the procedure of polymerization.

## 3. Results and discussion

For further improving the efficiency of the melt polycondensation for TLCPs, a second acetylating agent was proposed to continuously acetylate the phenolic hydroxyl in the monomers after complete consumption and removal of acetic anhydride and acetic acid with the increasing of the reaction temperature. PGAc was firstly considered for its lower reactivity towards carboxyl and more acetoxy groups in the same molecule, both beneficial to the possible acetylation. For assessing the acetylating ability of the second acetylating agent, a model reaction of PO and PGAc was firstly carried out.

As shown in Fig. 1, phenol and PGAc were mixed at r.t., where they were simply mixed physically and the corresponding  $^1\text{H}$  NMR showed clear signals with the same chemical shifts as for the individual molecules (SI Fig. 1). After keeping the temperature at 200 °C for 1 h, some PO transformed into the acetylated form (POAc), and most of the PGAc disappeared at the same time.  $^1\text{H}$  NMR was also used to interrogate the model reaction quantitatively (Fig. 2). The signal with the green triangle at 6.93 ppm ascribed to the hydrogen atoms of the benzene ring of PGAc decreased obviously after heating, and three series of new signals appeared marked by the dark blue nabla, purple diamond, and blue star, which were identified as signals of molecules derived from PGAc by losing one, two, and three acetoxy groups (PGAc-II, PGAc-I, and PG), respectively, indicating consumption of most of the PGAc. Meanwhile, another series of signals with yellow circles around 7.42 ppm, 7.26 ppm, 7.14 ppm, and 2.27 ppm originating from PO's acetylated derivative (POAc) were clearly observed, confirmed by the  $^1\text{H}$  NMR of POAc (SI Fig. 2). The changes in the  $^1\text{H}$  NMR of the mixture after heating at 200 °C for 1 h depicted the movement of the acetoxy group from PGAc to PO clearly, where PGAc could be regarded as a novel acetylating agent at high temperature. Further calculation showed about 83% of PGAc was

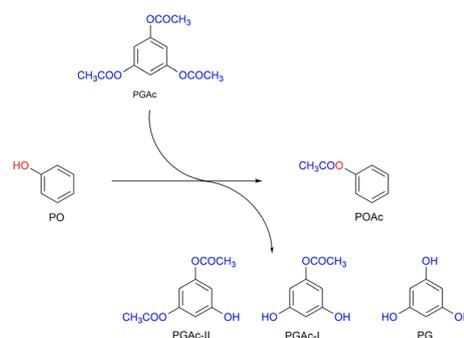


Fig. 1 Schematic diagram of the model reaction between PO and PGAc.



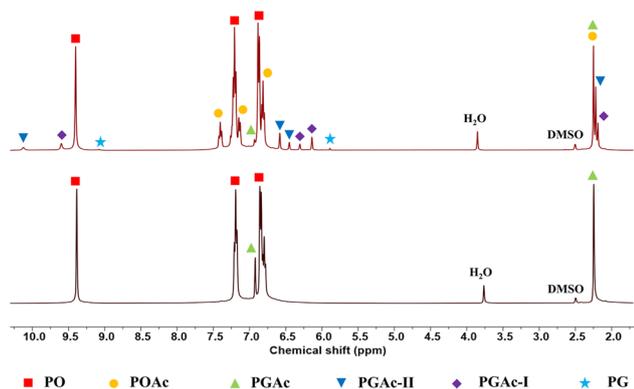


Fig. 2  $^1\text{H}$  NMR spectra of the mixture of PO and PGAc at r.t. (bottom) and after stirring at 200 °C for 1 h (top) (400 MHz,  $\text{DMSO}-d_6$ ).

transformed to 44% PGAc-II, 36% PGAc-I, and 3% PG, and only 17% PGAc remained, showing the strong acetylating ability of PGAc at 200 °C. Furthermore, it suggested that PGAc-II and PGAc-I also possessed the ability to further acetylate phenolic hydroxyls, where the relative strength of acetylation compared with PGAc were  $\sim 54\%$  for PGAc-II, and  $\sim 9\%$  for PGAc-I. Overall, PGAc showed both strong and continuous acetylating ability, and was an ideal agent to optimize the “one-pot” melt polycondensation of TLCPs.

With the novel acetylating agent in hand, polymerization to investigate the effect on the preparation of TLCPs was carried out. PGAc, as the second acetylating agent, was added to the polymerizing system for TLCPs together with the first acetylating agent, acetic anhydride (AA), and monomers (HBA and HNA), where AA transformed most of the phenolic hydroxyls to acetoxy groups at  $\sim 140$  °C and PGAc continuously acetylated the remaining phenolic hydroxyls at  $>200$  °C. As shown in Fig. 3, the preparation of a well-known TLCP, Vectra A950 containing 73 mol% HBA and 27 mol% HNA, was regarded as research objective to investigate the effect of the second acetylating agent, PGAc. PGAc was added in two ways, one was direct addition, and the other was by adding PG, which was transformed to PGAc by acetic anhydride, along with HBA and HNA. It is worth mentioning that the melt polycondensation of HBA and HNA could be conducted with a catalyst, imidazole (IMD) or  $\text{Zn}(\text{OAc})_2$ , or without catalyst.

Table 1 summarizes the TLCPs polymerized with different additives including catalysts, PG and PGAc. PGAc-TLCP-1 was prepared by the polycondensation of HBA and HNA with the help of IMD and PGAc, whose propagating rate was very large, as evidenced by the highest relative ratio of distillate (93.4%) before evacuation and the shortest time needed to complete the polycondensation (20 min). In contrast, examples no. 2 and no. 6–7 display the polycondensation with only PGAc or catalyst added, and they all proceeded slower than no. 1 with a smaller ratio of distillate and longer evacuation time. There was a synergistic effect between the catalyst and PGAc which was beneficial to the overall rate. Furthermore, the example with only IMD slowed more and only obtained a TLCP with a lower intrinsic viscosity (4.34) by pumping over 100 min, while the example with only PGAc could form a similar TLCP within a slightly longer period (25 min) compared with no. 1, suggesting that adding a large amount of PGAc could also play a significant role in polymerization even in the condition without catalyst. Furthermore, PG was investigated to see if it worked. PG-TLCP was obtained successfully with a slightly slower rate of propagation, but its color was blown, indicating more side reactions, oxidation and crosslinking, were happening (no. 5 in Table 1). Therefore, prior acetylation of PG was necessary for it to better act as a second acetylating agent.

We tried to better elucidate the essential reason for the difference in propagating rates by carefully analyzing the whole procedure of polymerization. Fig. 4b clearly showed the relationship between the ratio of distillate and evacuation time, where a higher ratio brought shorter reaction time and faster propagating rate, implying an accelerated acidolysis between acetoxy and carboxyl in the middle and last stages of polymerization. Meanwhile, addition of PGAc increased the rate of acidolysis compared to those with only catalyst, IMD or  $\text{Zn}(\text{OAc})_2$ . There should be two possible paths to effect acidolysis with PGAc. One was that PGAc turned the rest of the phenolic hydroxyls to highly active acetoxy groups and increased the concentration of active monomers, which largely contributed to the propagating rate. Another was that PGAc directly reacted with carboxyl and later served as a core to form a star-shaped TLCP, which had a lower possibility for the much lower reactivity of PGAc with carboxyl.<sup>17</sup> Furthermore, direct reaction of PGAc and carboxyl would limit the continuous propagation of

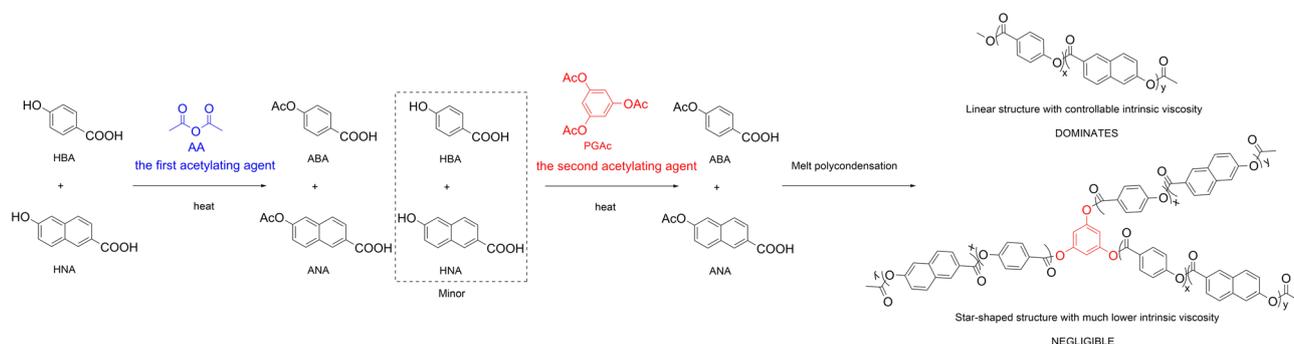


Fig. 3 Schematic diagram of melt polycondensation of HBA and HNA with a second acetylating agent.



Table 1 Synthesis and characterization of TLCPs

No.	Sample	Cat. <sup>a</sup>	Additive <sup>b</sup>	Ratio <sup>c</sup> (%)	Time <sup>d</sup> (min)	$[\eta]^e$ (dL g <sup>-1</sup> )
1	PGAc-TLCP-1	IMD	PGAc	93.4	20	5.06
2	PGAc-TLCP-2	—	PGAc	90.6	25	5.08
3	PGAc-TLCP-3	—	PGAc	— <sup>f</sup>	40	11.5
4	BA-TLCP	—	BA	— <sup>f</sup>	150	3.51
5	PG-TLCP	—	PG	86.9	40	4.92
6	TLCP-I	IMD	—	86.6	100	4.34
7	TLCP-Zn	Zn(OAc) <sub>2</sub>	—	83.2	100	4.55
8	TLCP-0	—	—	81.2	150	4.12

<sup>a</sup> The amount of catalyst was 200 ppm relative to the weight of the monomers. <sup>b</sup> The amount of additive was 0.3 mol%. <sup>c</sup> The ratio of the theoretical weight of the distillate containing acetic anhydride and acetic acid. <sup>d</sup> Vacuum sealing time during the period of melt polycondensation. <sup>e</sup> Tested in a 2.0 g L<sup>-1</sup> pentafluorophenol solution. <sup>f</sup> Not calculated.

chains, and the evacuation time needed for the specific intrinsic viscosity would be much longer than that observed here. We compared the intrinsic viscosities of the TLCPs by introducing PGAc or 1,3,5-benzenetricarboxylic acid (BA) with three carboxyls to prove that the direct reaction of PGAc with monomers is limited. A TLCP with a larger intrinsic viscosity (11.5, no. 3 in Table 1) could be obtained by slightly extending the reaction time (40 min) when introducing PGAc to the system. As a comparison, a TLCP with a much smaller intrinsic viscosity (3.51, no. 4 in Table 1) was obtained when replacing PGAc with BA even by polymerizing for 150 min, where BA served as a core to form star-shaped structures, much different from that when introducing PGAc. Therefore, the first path where PGAc worked as the acetylating agent should be the major one in the polymerization.

At the same time, curves of the ratio of distillate with time are displayed to further reflect the rate of acetylation by AA, where a higher value of the ratio at a certain moment reflects a faster rate and higher degree of acetylation below 200 °C (Fig. 4a). After reacting at 140 °C for 1 h, the temperature was increased from 140 °C to 300 °C at a rate of 1 °C min<sup>-1</sup>. The

period of 0–60 min in the curves of the distillate of PGAc-TLCP-1 and -2 were much higher than those of TLCP-I, TLCP-Zn and TLCP-0, indicating a faster rate of acetylation. PGAc might work as a bridge between AA and the acetylated monomer, like a kind of catalyst, which accelerates acetylation and then transfers the acetoxy groups to the monomers *via* transesterification. As time went on, the gap between the curves remained and became larger after 90 min, where a similar but more efficient distillation in the PGAc-assisted polymerization than that in TLCP-I was observed, and both of them did better than that of TLCP-Zn. Specifically, PGAc and IMD did better in the acetylation stage than Zn(OAc)<sub>2</sub> and led to a higher degree of acetylation, thus promoting the later step of polymerization. In contrast, although Zn(OAc)<sub>2</sub> was more efficient in acidolysis, it did not do as well at acetylation as IMD or PGAc,<sup>18</sup> which provided a worse basis and caused slower propagating as indicated by the smaller ratio of distillate (83.2%) and much longer evacuation time (100 min), only a little better than that without catalyst. Therefore, addition of PGAc was of much benefit to acetylation at first, and later displayed a more comprehensive impact on the synthesis of TLCPs. In a word, introduction of the novel acetylating agent,

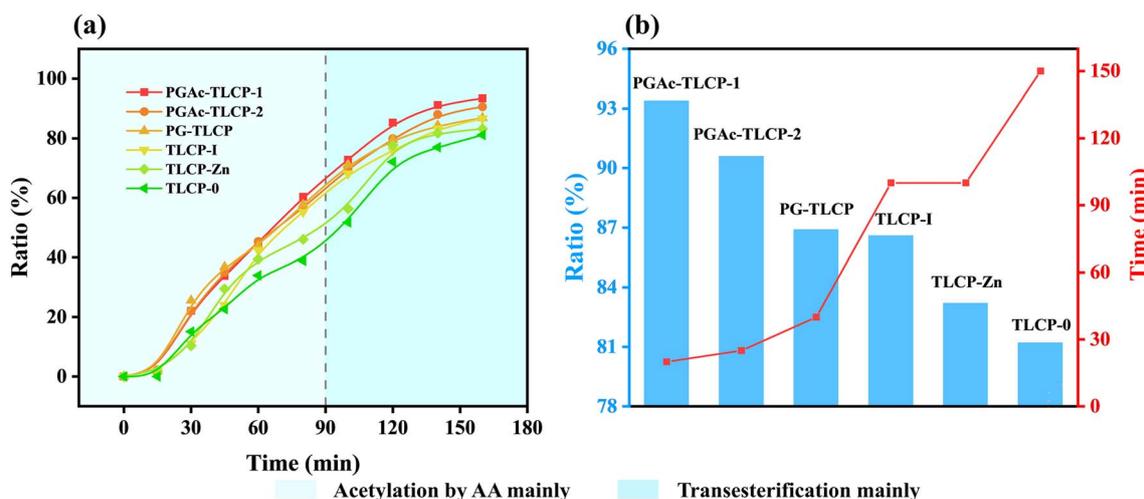


Fig. 4 (a) The ratio of distillate with time where the starting point was set at the time of the temperature increasing from 140 °C, (b) the ratio of distillate before vacuum sealing and vacuum sealing time of different melt polycondensations.



PGAc, could largely optimize the “one-pot” melt polycondensation of HBA and HNA, and even avoid use of a catalyst.

PGAc, as a novel acetylating agent derived from polyphenol, has been successfully applied in the preparation of TLCPs, which urged us to investigate if acetylates of other polyphenols work as well. As shown in Fig. 5, acetylates of RC, HQ, and BP, were chosen to be additives in the polycondensation of HBA and HNA without catalyst. It is worth mentioning that although the change in chain structure was ignored before for simplicity or was negligible for PGAc, we must admit that the acetylates we introduce here would insert in the middle and terminus of chains. The possibility of these acetylates inserting in the resulted chain by reacting with carboxyl could be quantified by the  $pK_a$  of their prototypes. The order of their  $pK_a$  values is PG < RC < BP < HQ, and the reactivity of the corresponding acetylates towards carboxyl is also PGAc < RCac < BPac < HQAc. Besides, the ability of the acetylates to acetylate the phenolic hydroxyl is opposite to that of the reactivity with carboxyl, leading to the order PGAc > RCac > BPac > HQAc.

As shown in Table 2, polycondensations of HBA and HNA with different additives all could proceed and the corresponding TLCPs, RCac-TLCP, BPac-TLCP, and HQAc-TLCP, were obtained successfully. The ratio of distillate and evacuation time of different polycondensations were the same as expected based on the above considerations, where RCac-TLCP propagated the fastest with a ratio of 89.2% and an intrinsic viscosity of 5.48 and was obtained within 30 min, and HQAc-TLCP formed slowly with a ratio of 84.7% and the smallest intrinsic viscosity of 5.02 was acquired after 90 min. A similar relationship between the ratio of distillate and evacuation time to Fig. 4b was found, suggesting these acetylates promoted polymerization by the same path as that for PGAc (Fig. 6b).

Furthermore, they had very similar curves for the ratio of distillate with evacuation time in both acetylation and acidolysis stages (Fig. 6a). But some differences in the values for acetylation were also observed, at the beginning of which the distillate for PGAc-TLCP-2 appeared slower than others. As we know, HBA and HNA would oligomerize partially to release some acetic acid, and a similar reaction also might occur for those acetylates with higher reactivity towards carboxyl and release more acetic acid than PGAc, causing the small differences in the curves of the distillate.

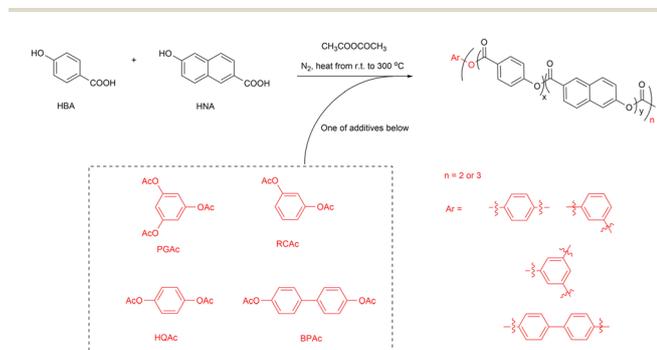


Fig. 5 Schematic diagram of melt polycondensation of HBA and HNA with different acetylating agents.

Table 2 Synthesis and characterization of TLCPs prepared with different acetylating agents

No.	Sample	Additive <sup>a</sup>	Ratio <sup>b</sup> (%)	Time <sup>c</sup> (min)	$[\eta]^d$ (dL g <sup>-1</sup> )
1	RCac-TLCP	RCac	89.2	30	5.48
2	BPac-TLCP	BPac	86.8	90	5.18
3	HQAc-TLCP	HQAc	84.7	90	5.02

<sup>a</sup> The amount of additive was 0.3 mol%. <sup>b</sup> The ratio of the theoretical weight of the distillate containing acetic anhydride and acetic acid.

<sup>c</sup> Vacuum sealing time during the period of melt polycondensation.

<sup>d</sup> Tested in a 2.0 g L<sup>-1</sup> pentafluorophenol solution.

It has been demonstrated that acetylates of polyphenols can be regarded as novel acetylating agents to further enhance the degree of acetylation of monomers and accelerate the rate propagation in “one-pot” melt polycondensation of TLCPs. It is worth mentioning that there is no modification of the operation procedures except additives, suggesting it could be directly applied in practical industrial production. Furthermore, these second acetylating agents we developed, including RCac, BPac, and HQAc, are all derived from commercially obtained compound, HQ, BP, and RC, which also are commonly used monomers in the production of commercial TLCPs, *e.g.* I-type TLCPs, suggesting no obvious increase in the cost and reliable stability in the production process of the TLCPs for potential application in industry.

The next step towards practical application of this strategy was to investigate the influence of inserting these acetylates on the properties of TLCPs, where different topologies might occur, including star-shape from PGAc, V-shape from RCac, and linear structure from BPac or HQAc. IR absorption spectra were recorded to analyse the possible differences in their chemical structures. They all had similar spectra from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>, implying similar chemical structures with each other, which were mainly derived from chains made of HBA (1598 cm<sup>-1</sup>) and HNA (1629 cm<sup>-1</sup>) (Fig. 7). Meanwhile, they were almost the same as that of Vectra A950, further supporting that the acetylates did not affect the chemical structure of the TLCPs (SI Fig. 3). There are two possible explanations for the consistency. One was that the amounts of the acetylates were all so low, ~0.3 mol%, that they couldn't be distinguished in the IR spectra.

The other was the lower possibility of successful insertion in chains since most of acetylates with lower reactivity towards carboxyl groups, *e.g.* PGAc and RCac, which would be removed under vacuum in the form of small molecules and thus show little influence on the TLCPs. Overall, although it couldn't be avoided that some of the acetylates inserted in chains *via* acidolysis with the carboxyls of monomers, the main characteristics of the chemical structures were still almost the same.

Thermodynamic properties, as one of the most significant characteristics of TLCPs, were also surveyed using TGA and DSC. As shown in Table 3, all the TLCPs had high thermostability with 5% mass loss temperature ( $T_{d,5\%}$ ) over 510 °C and maximum mass loss temperature ( $T_{d,max}$ ) over 530 °C, very near to those of Vectra A950. PGAc-TLCP-2 and RCac-TLCP were



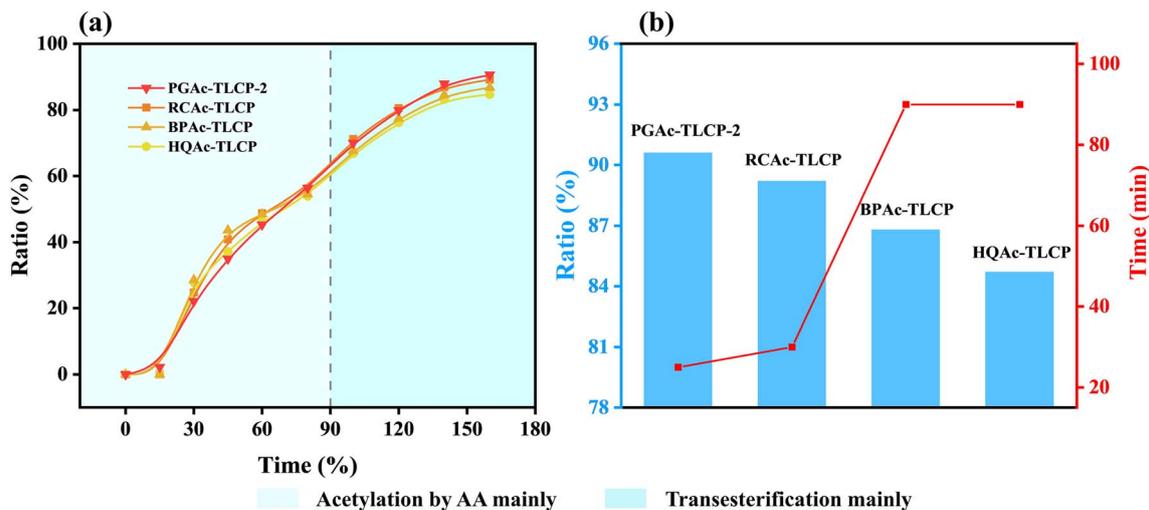


Fig. 6 (a) The ratio of distillate with time where the starting point was set at the time of the temperature increasing from 140 °C, (b) the ratio of distillate before vacuum sealing and vacuum sealing time of different melt polycondensations.

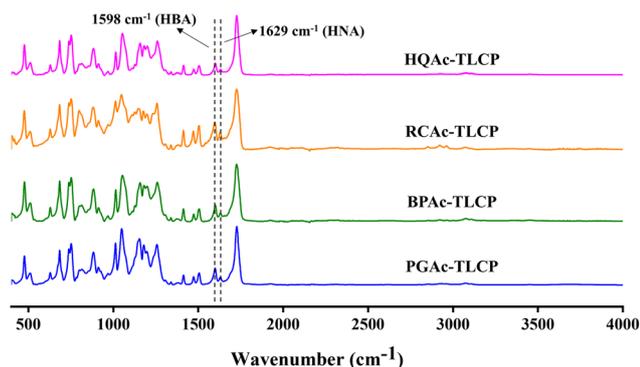


Fig. 7 IR spectra of TLCPs prepared by adding HQAc, RCAC, BPAC, and PGAc without catalyst.

Table 3 Thermodynamic properties of TLCPs prepared with different acetylating agents

No.	Sample	$T_{d,5\%}/^{\circ}\text{C}$	$T_{d,max}/^{\circ}\text{C}$	CY/%	$T_m/^{\circ}\text{C}$	$T_c/^{\circ}\text{C}$
1	PGAc-TLCP-2	511	531	41.6	286	235
2	RCAC-TLCP	511	531	42.2	281	238
3	HQAc-TLCP	522	538	44.2	282	236
4	BPAC-TLCP	522	538	44.5	281	238

slightly less stable than the others. Combined with lower residual carbon at 800 °C (CY), it was indicated that PGAc or RCAC might form more phenols after acetylating other phenolic hydroxyls of monomers which lowered the thermostability, as also evidenced by their TGA curves with different temperatures of obvious weight loss following the order of PGAc < RCAC < BPAC < HQAc (SI Fig. 4). Meanwhile, they all had melting peaks around 281 °C in their second heating curves in DSC (SI Fig. 5), very near to the classical melting temperature ( $T_m$ ) of Vectra A950. The possible star-shaped topology of PGAc-TLCP-2 with

a PGAc core further enhanced its  $T_m$  to 286 °C, and crystallization temperature ( $T_c$ ) was not affected, while the others with a V-shape and linear chains were not affected. In conclusion, these acetylates of polyphenols are not only good for the production of TLCPs with enhanced efficiency in the absence of catalyst, which avoided possible side reactions when processing and in usage, but also retained their main chemical structures and thermodynamic properties and showed great potential in practical industry.

## 4. Conclusions

Here, we developed a new strategy to significantly accelerate the efficiency of the production of TLCPs by introducing a second acetylating agent derived from some commercial polyphenols even without the help of a catalyst, which has potential to be directly applied in practical industry with an unchanged process flow and unaffected thermodynamic properties.

In the study, PGAc showed a strong ability for acetylation of phenol in the model reaction at high temperature (200 °C), where the commonly used acetylating agent, acetic anhydride, had been removed *via* evaporation. PGAc worked as a second acetylating agent at high temperature and largely speeded up the distillation of acetic acid and the efficiency of the melt polycondensation. Furthermore, acetylates of other polyphenols were found to have a similar influence on the preparation of TLCPs, *e.g.* RCAC, BPAC, and HQAc. The resulting TLCPs had almost the same chemical structures and thermodynamic properties, which were also similar to the well-known commercial TLCP, Vectra A950, highlighting the importance of the theory and application.

Furthermore, the strategy also opens a new route to the terminal functionalization of TLCPs for more applications in heat treatment, solid state polycondensation, composite materials, and so on, which are being carried out in our laboratory now.



## Author contributions

Conceptualization, H. Z.; data curation, H. Z., X. S. and S. S.; formal analysis, H. Z.; funding acquisition, Q. L.; investigation, H. Z.; supervision, Q. L.; validation, H. Z.; visualization, H. Z. and X. S.; writing—original draft, H. Z.; writing—review and editing, H. Z. and X. S.; All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information (SI). Supplementary information: the  $^1\text{H}$  NMR spectra of the second acetylating agents. See DOI: <https://doi.org/10.1039/d5ra07423a>.

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