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A Facile Synthetic Route to Poly(*p*-phenylene terephthalamide) with Dual Functional Groups

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Claisen rearrangement reaction was employed for the first time to obtain a novel PPTA bearing reactive allyl and hydroxyl groups, that may act as a sizing agent of Kevlar fiber to improve the interface structure and interfacial
10 **adhesion of rubber or epoxy based composites.**

Poly(*p*-phenylene terephthalamide) (PPTA) is a famous aramid polymer. Its totally aromatic, rod like structure facilitates the fabrication of fibers (e.g. Kevlar) with a very high orientation from a liquid crystalline solution.[1] These fibers have ultrahigh
15 tensile strength and modulus, exceptional heat and flame resistance as well as chemical, solvent and environmental stabilities, and have been used as reinforcing materials of composites in wide applications such as military, aeronautics, astronautics, automobiles, and sports.[2-6]

20 One main challenge in manufacturing high performance composites reinforced by Kevlar fibers is their low affinity for interfacial adhesion towards resin matrix due to the highly oriented, extended-chain morphology and the lack of reactable substituent. It is a common practice to introduce substituents on
25 PPTA chains through either amide groups or phenyl rings to overcome this difficulty. The *N*-substitution of amide group works at the cost of damaging interchain hydrogen bondings.[7] The substitution on phenyl ring does not have such a drawback and therefore has been extensively investigated. The substituents
30 employed include alkyl,[8-10] aryl,[11-13] halogen,[8,14] nitro,[15,16] sulfo,[17-20] hydroxyl,[21] propargyl,[22] and other groups. However, all these chemically modified PPTAs contain only mono-functional groups, which are just effective to one type matrix, e.g. rubber or epoxy. It is highly desired to develop a facile method to obtain
35 PPTA with dual functional substituents, which may act as a reinforcing material alone or a sizing agent of Kevlar fiber to improve the interface structures and interfacial adhesions of composites based on various resins such as rubber and epoxy.

Claisen rearrangement (**CR**) is a powerful and mild carbon-
40 carbon bond-forming chemical reaction.[23] The aromatic variation with allyl phenyl ether has the advantage of introducing allyl and hydroxyl groups on phenyl ring simultaneously, but has never been applied in the preparation of high performance polymer. Herein, we report the synthesis of a novel PPTA bearing both
45 apolar allyl and polar hydroxyl groups via low temperature polycondensation of *p*-phenylenediamine (PPD) with 2,5-diallyloxy-terephthaloyl chloride (**V**) and subsequent thermally induced **CR**.
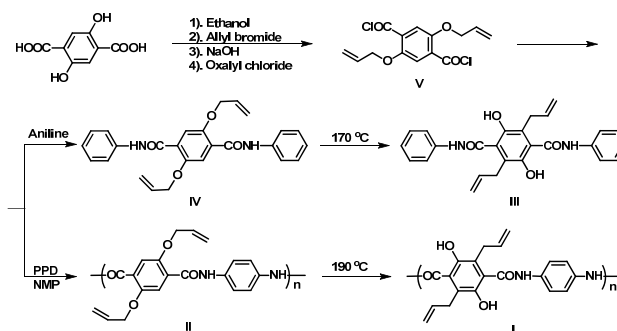
50 **Scheme 1** Syntheses of model compounds and polymers

The monomer **V** was obtained from inexpensive, commercially available 2,5-dihydroxyterephthalic acid through esterification with ethanol, etherification with allyl bromide, hydrolization under alkaline condition, and chloroformylation by oxalyl
55 chloride (Scheme 1). All the reactions happened in high yields and the intermediates and products were easily purified by recrystallization. To test the feasibility of synthetic strategy and help characterize the structure of target polymer, 2,5-diallyloxy-*N,N'*-diphenylterephthalamide (**IV**) was first prepared as a model
60 compound by the amidation of **V** with aniline and then subjected to **CR** at 170 °C, which was monitored by NMR and FTIR spectroscopy. Figure 1 presents ^{1}H NMR spectra of **IV** annealed at 170 °C for various time. The assignment of each resonance peak was made by Heteronuclear Multiple Quantum Coherence
65 (HMQC) and Heteronuclear Multiple Bond Correlation (HMBC) (Figs. S1 and S2). The resonance absorptions at 7.47 ppm were attributed to the aromatic protons (e) of central phenyl ring and 4.73 ppm for the methylenic protons (f) of allyloxy group, respectively. As **CR** continued, these two absorptions became
70 weak and disappeared completely after 6 h. Meanwhile, two new absorptions from benzylic protons (f') and hydroxyl protons (e') at 3.36 and 8.25 ppm, separately, were observed, implying the formation of 2,5-diallyl-3,6-dihydroxy-*N,N'*-diphenylterephthalamide (**III**). Although the resonance peaks of
75 other protons of **IV** did not change remarkably during **CR**, the signals of vinylic protons shifted upfield. The ^{13}C NMR and FTIR spectra gave the consistent results (Figs. S3 and S4).

The polycondensation of **V** and PPD was carried out in *N*-methyl-2-pyrrolidone (NMP) solution containing 8 wt% CaCl$_2$ at
80 -10 °C. Due to the tight wrapping of high population of apolar allyloxy groups,[10] which requires distinct solvent to polar main

chain, the resultant polymer **II** was insoluble in either concentrated H_2SO_4 or common organic solvents. It was therefore not possible to characterize its molecular weight by means of viscometry applied for PPTA and other techniques. To increase
[5] its solubility, *N*-butylation was carried out with Katayose's method.[7] The derived polymer showed number-averaged molecular mass (M_n) of 9100 Dalton and molecular mass polydispersity index (PDI) of 1.79, estimated by gel permeation chromatography using tetrahydrofuran as an eluent.
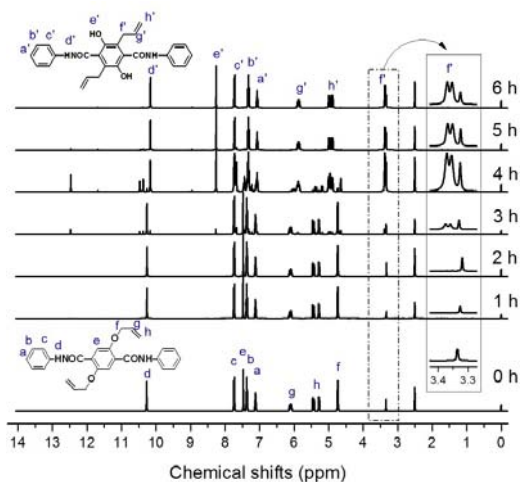

[10]

Fig.1 ^{1}H NMR spectra of model compound **IV** annealed at 170 ºC for various time. Measured in d6-DMSO at room temperature.

The **CR** reaction of **II** was carried out in NMP at 190 ºC for various time under inert atmosphere. The presence of hydroxyl
[15] groups enabled the target polymer **I** to dissolve readily at room temperature in NMP, dimethyl formamide, dimethyl sulfoxide (DMSO), *m*-cresol, and concentrated H_2SO_4 (Table S1). Before the reaction began, **II** was suspended in NMP as fine powders. As **CR** proceeded, the solids became smaller gradually and clear
[20] solution was obtained after 3 h. The reaction was allowed to continue for another 3 h to make sure completion. Since **II** was insoluble, solid state NMR spectroscopy was employed to monitor the reaction process. Fig. 2 displays solid state ^{13}C NMR spectra of **II** annealed at 190 ºC for 2, 4, 6 and 8 h, respectively,
[25] together with PPTA. The assignment of each resonance peak was made according to those of the model compound (Fig. S5) and PPTA.[24] For **II**, the peak at 157 ppm was attributed to the carbon atom of carbonyl group, whereas that at 147 ppm to the carbon atom on the phenyl ring linked to the ether oxygen atom. The
[30] methylenic carbon of allyloxy group gave a peak at 68 ppm. After **CR**, the signals belong to carbon atom of amide group shifted downfield to 164 ppm due the decreased shielding effect of *ortho* substituents. The benzylic carbon atom showed absorption at 28 ppm. The absence resonance peaks at 68 and 147 ppm suggested
[35] that the polymer **II** was completely converted to the polymer **I**. The proton NMR of rearranged samples in deuterated DMSO gave a consistent conclusion (Fig. S6).

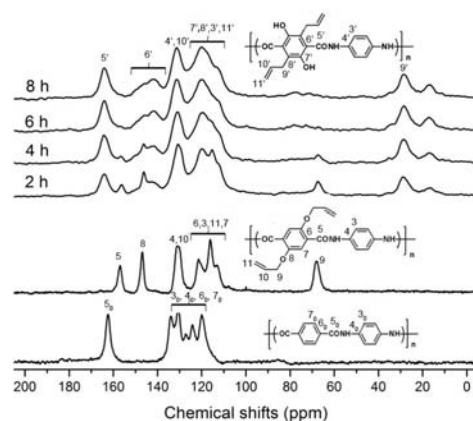[40] **Fig.2** Solid state ^{13}C NMR spectra of polymers PPTA and **II** annealed at 190 ºC for 2, 4, 6 and 8 h.

The structures of **II** and **I** were also confirmed by FTIR (Fig. S7). The absorptions at 1193 and 1000 cm⁻¹, attributed to the symmetrical and asymmetrical stretching vibrations of ether bond
[45] C-O-C of **II**, respectively, vanished after rearrangement reaction. Whereas **I** displayed a broad absorptions centered at 3000 cm⁻¹ typically for hydroxyl group and the bending vibration of O-H bond at 1320 cm⁻¹. A new absorption at 1166 cm⁻¹ due to the stretching vibration of C-OH bond was also observed.
[50] The polymers **I** and **II** were quite thermal stable and had temperature of 5wt% loss under nitrogen atmosphere above 360 ºC (Fig. S8). Fig. 3 exhibits differential scanning calorimetry (DSC) curves of **II** recorded during first and second heating scans. The first heating curve displays a large exothermic peak centered
[55] at 220 ºC, which was attributed to **CR** reaction. However, no discernible phase transition was observed on the second heating curve, implying the complete conversion from **II** to **I**. This provided another tool to track **CR** process of **II**.
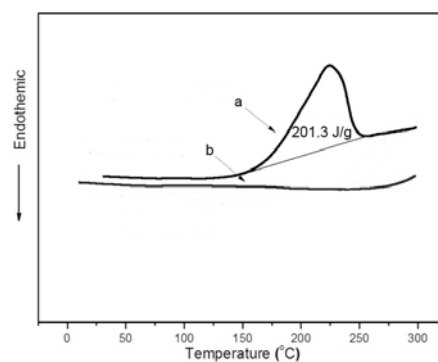
[60]

[65]

[70]

Fig. 3 DSC curves of II recorded during first (a) and second (b) heating scans. Heating rate: 5 ºC/min; atmosphere: N_2.

The simultaneous introduction of allyl and hydroxyl groups not only improved the solubility of PPTA but also changed its surface
[75] property and intermolecular packing manner. Fig. 4 exhibits the images of water droplets on the surfaces of PPTA and **I** films, respectively. Because of the dense substitution of polar hydroxyl groups, the polymer **I** showed a smaller contact angle of 62º than PPTA (72º), an indicative of increase in affinity to water. In the
[80] powder wide-angle X-ray diffraction pattern (Fig. 5), **II** presented an intensive peak at $2\theta = 9.2$º in the low angle region and another one at $2\theta = 26.3$º in the wide angle region. In addition, two

shoulder peaks at $2\theta = 18.4$ and $21.0°$, respectively, existed. A highly ordered aggregated structure of macromolecules was implied. After **CR**, **I** showed only two diffused halos in the low and wide angle regions, separately, suggesting an amorphous nature. The patterns of both polymer **I** and **II** were totally different from that of PPTA,[25] indicating the remarkable roles of side groups. It should be noted that although PPTA is a lytropic liquid crystalline aromatic polyamide, the polymer **I** generated no mesophase. It is probably due to the highly crowded substituents around polymer backbone.
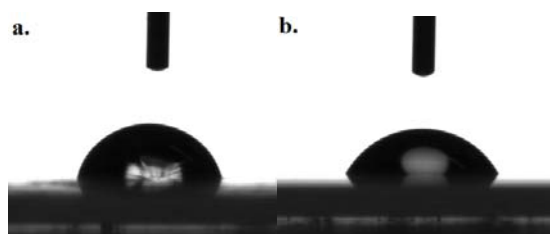

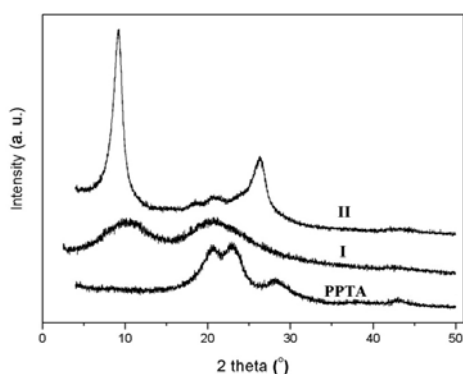**Fig. 4** Water droplets on the films made up of (a) PPTA and (b) **I**

Fig. 5 Wide angle X-ray diffraction curves of polymers **II**, **I**, and PPTA

One potential utility of **I** is to improve the interface structures and interfacial adhesions of Kevlar fiber reinforced composites, as the sizing agent or as a reinforcing material alone, through the reactions of allyl and hydroxyl groups with rubber and epoxy, respectively. To demonstrate such an application, the interface property of Kevlar fiber-rubber composite was studied by single fibre pull-out force method. Under identical and un-optimized conditions, the pullout force of fibers treated with as low as 0.1 and 0.5 wt% solution of **I** in NMP was 25.0 and 30.1 N, respectively, obviously larger than that of the fiber without treatment (20.8 N) (For details, see supporting information).

In summary, we reported a facile and efficient method to prepare a novel PPTA bearing both apolar allyl and polar hydroxyl groups by a combination of the step-growth polymerization and subsequent **CR**. The rearrangement processes of the model compound, **IV**, and the precursor of target polymer, **II**, were completed in 6 h at 170 °C for the former while at 190 °C for the latter without addition of any catalyst as monitored by NMR and FTIR. This polymer showed a remarkably improved solubility and hydrophilicity, and may find applications in rubber or epoxy resin based high performance composite acting as a reinforcing material alone or a sizing agent of Kevlar fiber. The strategy of introducing simultaneously two kinds of reactive groups to polymer backbone, developed in the present work, should also be applicable to other aromatic engineering polymers by improving the interface structures and interfacial adhesions. The corresponding work is under way.

Notes and references

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† Electronic Supplementary Information (ESI) available: [The experimental details, ^{13}C NMR and FTIR spectra of model compound and its product of Claisen rearrangement reaction, the solubilities, thermal properties and single fibre pull-out force test results of polymers]. See DOI: 10.1039/b000000x/
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