

## Supporting information

### Novel nanocellular poly(aryl ether ketone) foam fabricated by controlling the crosslinking degree

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#### Synthesis of Polymers

Synthesis of poly(aryl ether ketone) containing lateral carboxylic acid groups (acid-PAEK)

4,4'-Bis(4-hydroxyphenyl)pentanoic acid (5.7264 g, 0.02 mol), 4,4'-difluorobenzophenone (4.3640 g, 0.02 mol),  $K_2CO_3$  (4.1400 g, 0.03 mol), dimethyl sulfoxide (DMSO) (40 mL) and toluene (20 mL) were added to a 100 mL three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, a condenser, a thermometer and a nitrogen inlet. Under a nitrogen atmosphere, the mixture was heated to 130-140 °C and maintained at that temperature for 3 h to dehydrate the system by means of a Dean-Stark trap through toluene. After dehydration and removal of the toluene and water, the poly condensation reaction was continued for 4-6 h at 150 °C. Then, the viscous solution was slowly poured into water and stirred vigorously. The threadlike polymer was pulverized, and the resulting powders were washed several times with hot deionized water and ethanol and dried at 80 °C under vacuum for 24 h. yield: 92%.

Synthesis of poly(aryl ether ketone) containing naphthalene pendants on the side chains (NA-PAEK)

DMAP (0.0732 g, 0.6 mmol) and 1-naphthol (0.864 g, 6 mmol) were added to a solution of the acid-PAEK (1.84 g) in 50 mL anhydrous tetrahydrofuran. Then a solution of DCC (1.24 g, 6 mmol) in anhydrous tetrahydrofuran was added into the mixture drop by drop. The mixture was stirred at room temperature for 72 h. The product was filtered to remove dicyclohexyl urea and put into alcohol to precipitate. The obtained polymer powders were further purified by reprecipitation in alcohol and dried at 60 °C under vacuum for 24 h. Yield: 77%.

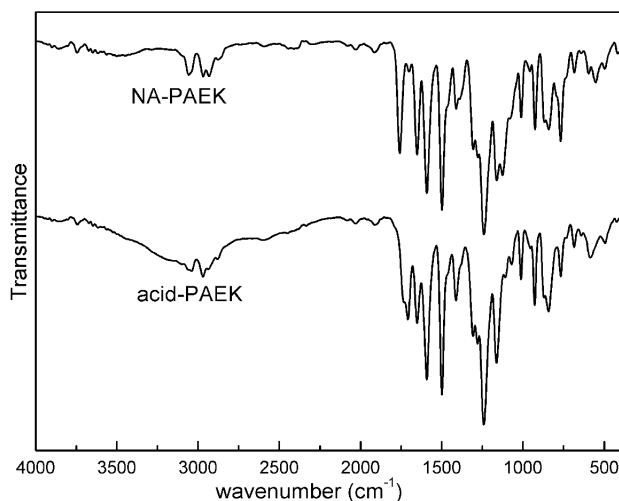
#### Characterization of polymers

The polymer was synthesized by attaching the 1-naphthol pendant to the acid-PEEK using a classical esterification with DCC and DMAP as catalyst at room temperature. The FT-IR spectra of NA-PAEK and acid-PAEK (Fig.SI1) show that the absorption bands of the carboxyl groups at 1700  $cm^{-1}$  and 1730  $cm^{-1}$  tend to disappear as well as the absorption band of ester-carbonyl groups at 1763  $cm^{-1}$  appears after esterification. From the  $^1H$ NMR spectra it can be discovered that the NA-PAEK exhibits seven new peaks at 7.0-8.0 ppm corresponding to the chemical shift of

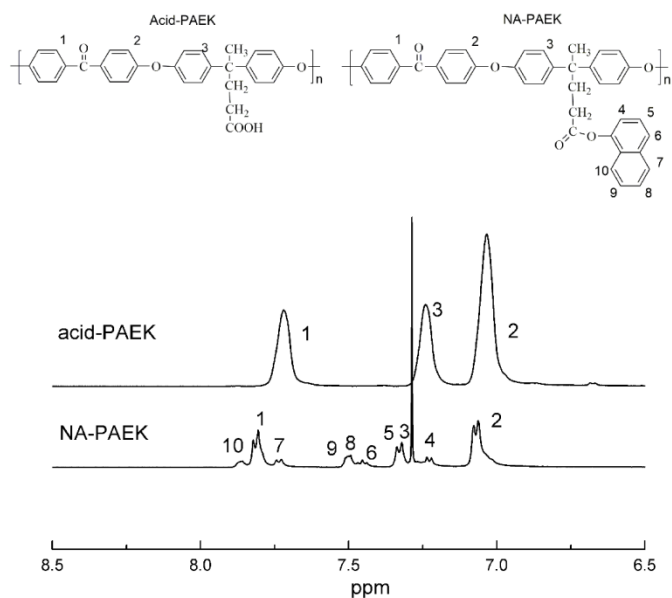
hydrogen in naphthalene pendant compared with the acid-PAEK (**Fig.SI2**). These changes indicated the successful introduction of the naphthalene pendant to the matrix polymer.

The DSC curve of NA-PAEK samples are shown in **Fig.SI3**. It can be seen that the Tgs of the samples with low and higher crosslinking degree (Gel 18% and Gel 48%) change little compared with uncrosslinked one (Gel 0%), while Tg of the sample with high crosslinking degree (Gel 95%) increases from 141 °C to 153 °C.

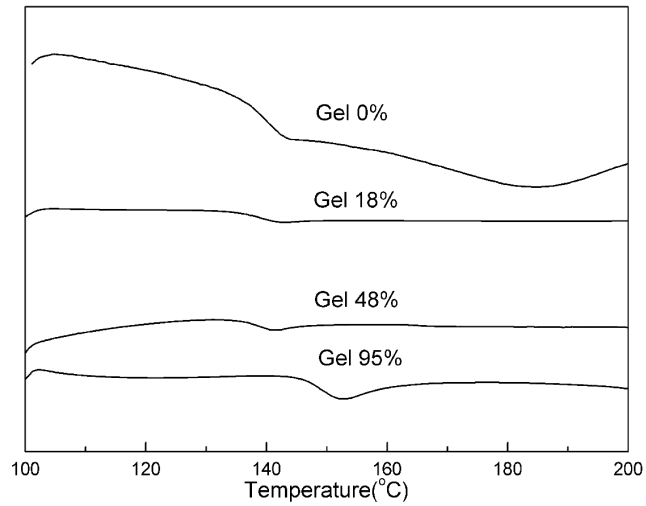
The testing process of gel content for NA-PAEK films after crosslinking has been shown in **Fig.SI4**.



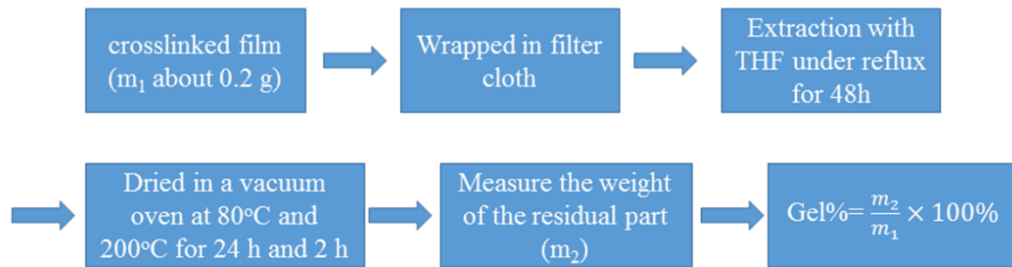
**Fig.SI1** FT-IR spectrum of NA-PAEK and acid-PAEK



**Fig.SI2** <sup>1</sup>H NMR spectrum of acid-PAEK and NA-PAEK



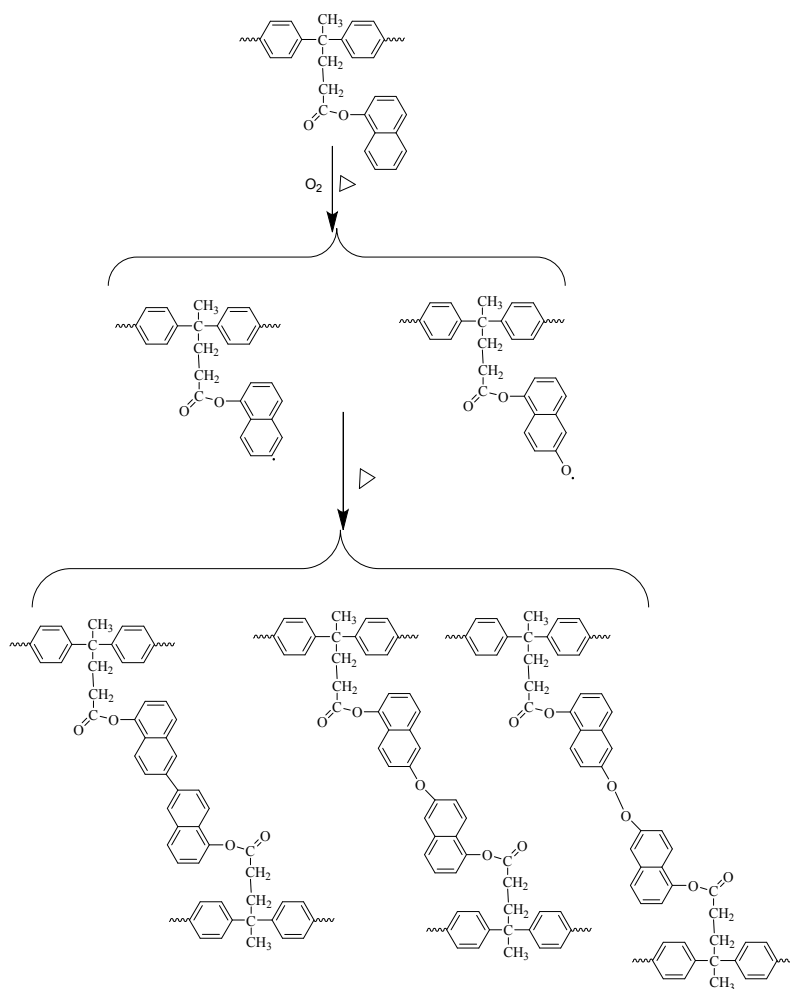
**Fig.SI3** DSC curve of NA-PAEK samples with different gel content



**Fig.SI4** The testing process of gel content for NA-PAEK films after crosslinking

## Crosslinking mechanism

The crosslinking mechanism for NA-PAEK could be found in **Scheme.SI1**.



**Scheme.SI1** The crosslinking mechanism for NA-PAEK.