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Synthesis of High-Performance Polymers *via* Copper-Catalyzed Amination of Dibromoarenes with Primary Aromatic Ether Diamines

Zhenfang Shang, Li Yang*, and Guanjun Chang*

State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials & School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang, 621010, P. R. China.

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Abstract: In this paper, we introduce three high-performance polymers with similar structures, poly(imino ether ketone) (PIEK)s, which are synthesized by the ligand free copper-catalyzed C-N cross coupling reaction of aryl halides and primary aromatic diamines at moderate temperature. The influence of the solvents, base, temperature, and catalyst ligands on the polycondensation reaction is investigated. The structures of the polymers are characterized by means of ^{1}H NMR spectroscopy, FTIR spectrometer and elemental analyses, and the results show a good agreement with the proposed structure. They all exhibit high glass transition temperature (T_g>170 ºC), good thermal stability with high decomposition temperature ($T_{d,5\%}$>440 ºC), and an excellent solubility in most organic solvents. In view of its good thermal stability and solubility, PIEK-1 foam with low density, 96 mg/cm^3, is prepared *via* thermal induced phase separation and freeze-drying technology. The PIEK-1 foam possesses higher thermal stability than that of basal PIEK-1 ($T_{d,5\%}$>465 ºC). Furthermore, due to intermolecular hydrogen bonds of the polymers, the achieved foam exhibits good mechanical property.

Keywords: poly(imino ether ketone)s, heat-resistant polymer, copper-catalysis, foam.

Introduction

With the development of the modern advanced science and technology, the demand for heat resistant material is becoming more and more urgent. For many years, scientists around the world are searching for new technology and new method in this field. Heat resistant polymer rises in response to the proper time and conditions and becomes the focus of attention.[1-3] Especially, as one of the most promising class of heat-resistant engineering polymers, poly(ether ether ketone) (PEEK) is widely applied due to the outstanding properties, such as thermal stability and chemical stability.[4,5] However, the availability of such polymers is limited to a certain extent for a variety of reasons, such as the relatively low glass transition temperature (T_g) and poor solubility. Despite of much research efforts dedicated to the structural modification,[6-8] the development of a new strategy for construction of soluble and heat-resistant polymer materials through chemical polymerization is still an attractive and promising goal.

Among the examples reported, the Pd-catalyzed C-N cross coupling reaction, which has been applied to a great amount of new materials,[9,10] is definitely a highly effective candidate. And we have synthesized a series of novel high-performance polymers *via* palladium-catalyzed polycondensation (Hartwig-Buchwald reaction) of aromatic dichloro or dibromo ketones with various aromatic diamines.[11-14] However, after years of research about palladium catalysis, scientists gradually realize some of the shortcoming of it, including toxicity, high cost, air-sensitivity and the dependence to unstable and toxic organic phosphine ligands. In view of these drawbacks of palladium catalysis, the application of the resulting polymers is limited. And the development of a mild and efficient method is still highly desirable. So the venerable copper-catalyzed coupling reactions return to the limelight.[15-17] A copper-catalyzed coupling reaction is an alternative procedure with low cost and can be utilized under mild condition. In addition, many reports also revealed that compared to other transition-metal catalysts, copper-catalysts are inexpensive, readily available, insensitive to air, and can be easily handled.[18-21] Recently, the catalytic amination reaction of arylene halides with primary amines using copper complexes has become a significant synthetic procedure for a variety of arylene amines, but there are hardly any reports about its application in the construction of polymers. Herein, our aim is to use this method for developing new conditions for copper-catalytic C-N coupling reaction and apply them to heat-resistant and soluble high performance polymers. In this paper, a series of aromatic poly(imino ether ketone)s (PIEKs) have been obtained by the polycondensation of dibromo ketones and primary aromatic diamines using the catalytic

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*Corresponding Authors. E-mails: yanglichem628@126.com or gjchang@mail.ustc.edu.cn

system generated from CuO nanoparticles and KOH. The use of inexpensive copper-catalysts instead of expensive palladium-catalysts is, as has already been shown for poly(imino ketone)s (PIKs),[10,11] very attractive for obtaining aromatic polymers. Due to their unique micropore configuration, excellent mechanical, optical, thermal, acoustical and other properties, low density polymer foam materials can be used for acoustic insulation, heat insulation, integrated circuit substrate, catalyst carriers, gas and liquid filter and other materials, thus they have extensive application prospective in high technology, building, industries, aerospace, biotechnology, packaging and other fields.[22-25] However, the preparation of heat resistant low density polymer foam is limited due to the poor solubility of the traditional high performance polymers. In this paper, the low density PIEK foam was prepared *via* thermal induced phase separation and freeze-drying technology. Meanwhile, the thermal and mechanical properties were also investigated in details.

Experimental

Materials. 4,4'-Dibromobenzophenone and 4,4'-oxydianiline were purchased from J & K Technology. 1,4-Bis(4-bromobenzoyl) benzene was synthesized in the laboratory. 1,4-Bis (4-aminophenoxy) benzene was purchased from Daikin Fine Chemical Laboratory, Ltd, Toshima, Kita-ku, Tokyo, Japan. CuI and CuO nanoparticles (particle: 33 nm surface area: 29 m^2/g) were purchased from WanJing New Material Co., Ltd in hangzhou. The rest materials and reagents were obtained from different commercial sources and used without further purification.

Measurements. FTIR spectra was recorded on a Nicolt 6700 FTIR spectrometer. ^1H NMR was performed on AVANCE 300 MHz NMR spectrometers in dimethylsulfoxide (DMSO)-d_6. The elemental analysis characterization technique was measured on a Vario EL III apparatus. Thermo gravimetric analysis was performed on a Setarma TG-92 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The glass transition temperature was obtained by DSC curves at a rate of 10 °C min^{-1} under flowing nitrogen gas. Gel permeation chromatography (GPC) analysis was carried with a Wyatt DAWN HELEOS using *N,N*-dimethylformamide (DMF) (adding 1% LiBr) as eluent, testing temperature 50 °C. The morphology was observed by a scanning electron microscope (KYKY-1000B).

Synthesis of Phenyl-(4-phenylamino-phenyl)-methanone. A typical synthesis procedure for phenyl-(4-phenylamino-phenyl)-methanone is illustrated as an example. To a flame-dried Schlenk test tube with a magnetic stirring bar was charged (4-bromo-phenyl)-phenyl-methanone (1.0 mmol), aniline (1.0 mmol), CuO nanoparticles (0.2 mmol), DMSO (3 mL) and KOH (2.0 mmol) under N_2 (Scheme II). The system was then evacuated twice and back filled with N_2. The Schlenk was immersed in a 110 °C oil bath for 24-48 h with continuous stirring. The resulting solution was allowed to slowly cool to room temperature, diluted by DMSO, and filtered through Celite to remove the catalyst. The filtrate was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and the resulting residue was purified by column chromatography on silica gel to provide the yellow product. Yield: 92%; ^1H NMR (300 MHz, DMSO-d_6): δ=8.90 (s, 1H), 7.55-7.52 (m, 2H), 7.35-7.31 (m, 2H), 7.22-7.20 (d, J=7.6 Hz, 2H), 7.11-7.09 (d, J=8.8 Hz, 2H), 7.02-6.98 (m, 1H); Anal. for $(C_{19}H_{15}NO)_n$ $(273.33)_n$: C, 83.52; H, 5.49; N, 5.13; Found: C, 82.06; H, 5.61; N, 5.10.

Synthesis of Poly(imino ether ketone)s. A typical synthesis of PIEKs was conducted in a two-necked flask (50 mL) equipped with a magnetic stirrer, a nitrogen outlet, inlet, and water-cooled condenser. Aryl halides (4.0 mmol), primary aromatic diamines (4.0 mmol) copper-catalyst (0.8 mmol), DMSO (10 mL) and KOH (8.0 mmol) were added to this flask (Scheme III). Then the reaction mixture was rushed with high purity nitrogen. The flask was immersed in a 110 °C oil bath for 24-48 h with continuous stirring. Next, the resulting polymer solution was allowed to slowly cool down to room temperature, diluted by DMSO, and filtered through Celite to remove the catalyst. The filtrate was subsequently poured into cool water, the precipitate which formed was isolated by filtration and rinsed with both water and methanol for several times, filtered and dried at 100 °C under vacuum.

PIEK-1: Yield: 87%; FTIR spectrum (KBr pellet, cm^{-1}): 3387 (N-H), 1591 (C=O), 1282 (C-N); ^1H NMR (300 MHz, DMSO-d_6): δ=8.61 (s, NH), 4.94 (s, NH_2), 7.32-6.04 (m, C_6H_4); Anal. Calcd for $(C_{25}H_{18}N_2O_2)_n$ $(378.42)_n$: C, 79.35; H, 4.79; N, 7.40; Found: C, 79.53; H, 4.72; N, 7.37.

PIEK-2: Yield: 91%; FTIR spectrum (KBr pellet, cm^{-1}): 3386 (N-H), 1622 (C=O), 1260 (C-N); ^1H NMR (300 MHz, DMSO-d6): δ=8.57 (s, NH), 4.94 (s, NH_2), 7.53.-6.54 (m, C_6H_4); Anal. Calcd for $(C_{32}H_{22}N_2O_3)_n$ $(482.53)_n$: C, 79.67; H, 4.56; N, 5.81; Found: C, 79.58; H, 4.62; N, 5.78.

PIEK-3: Yield: 94%; FTIR spectrum (KBr pellet, cm^{-1}): 3346 (N-H), 1619 (C=O), 1304 (C-N); ^1H NMR (300 MHz, DMSO-d_6): δ=8.94 (s, NH), 5.23 (s, NH_2), 7.66-6.21 (m, C_6H_4); Anal. Calcd for $(C_{38}H_{26}N_2O_4)_n$ $(574.62)_n$: C, 79.44; H, 4.53; N, 4.88; Found: C, 79.38; H, 4.56; N, 4.86.

Preparation of PIEK-1 Foams. PIEK-1 was dissolved in 1,4-dioxane at 70 °C. Considerable air bubbles were trapped in the frozen body, resulting in relatively large holes in the PIEK-1 foams, the ultrasonic method was used to treat the PIIK solution for purpose of deaeration. The deaeration period was 5 min with a frequency of 100 kHz. The cooling rate was 100 K/min. Then, a freeze-drying apparatus was used to dry the PIEK-1 foams. The vacuum degree was controlled at 0.1 mba under the room temperature for 72 h. After drying, the foam samples were taken out to measure on density, and then the foams were sealed and kept in a dessicator.

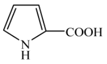
Results and Discussion

Design and Synthesis of Polymers. Because of the high surface area and reactive morphologies, nanomaterials have been accepted as effective catalysts for organic synthesis. Herein, we wish to present cross-coupling reaction of aryl halides and primary aromatic diamines with the CuO nanoparticles as a catalyst to give the corresponding polymers in good yields. On the basis of prior observations, a tentative catalytic cycle was proposed (Scheme I). The reactions occur *via* oxidative addition followed by a reductive elimination process. First, the DMSO-stabilized CuO nanoparticles[15,20] with a high surface area may undergo oxidative addition of the aryl bromide to form the oxidative addition complex I where the excess positive charge generated could be shared among the CuO nanoparticles present on the surface of the cluster. Then the intermediate II would be formed in the presence of nucleophile aromatic amine and KOH, which undergoes reductive elimination to form the cross-coupled product III.

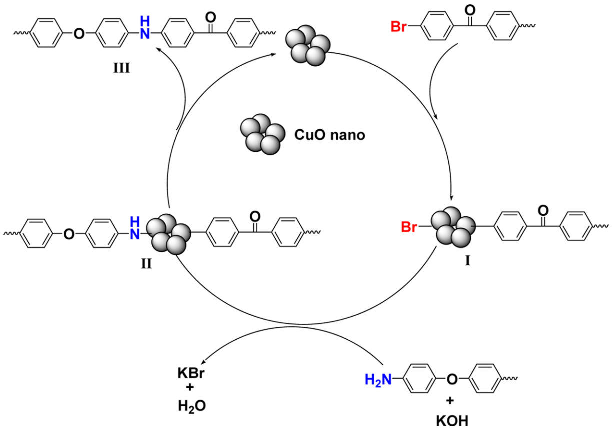
To investigate the potential of the amination reaction for a polycondensation process, phenyl-(4-phenylamino-phenyl)-methanone was synthesized as a model compound by a copper-catalyzed amination of (4-Bromo-phenyl)-phenyl-methanone with aniline as a primary aromatic amine (Scheme II).

The effect of different catalyst systems on yield of phenyl-(4-phenylamino-phenyl)-methanone is shown in Table I. CuO nanoparticles as a effective copper-catalyst brought a higher yield than CuI even compared with the ligand combined one (Table I, entries 1-3). The use of DMF as the solvent instead of DMSO, led to a dramatically decreased yield (14%) while the use of DMAc lowered the yield to 23% (Table I, entries 4-5). When NaO$_t$Bu was used as a base, phenyl-(4-phenylamino-phenyl)-methanone was produced in 68% yield, and when NaOH was utilized, the product was hardly obtained with only a 6% yield (Table I, entries 6-7). It was obviously to see that the combination of CuO nanoparticles, DMSO and KOH showed the best catalytic activity, and a higher yield was obtained.

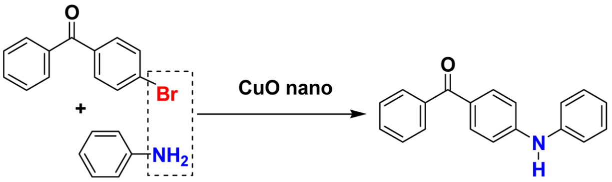
Table I. Effect of Different Catalyst Systems on the Yield of the Products[a]

Entry	Copper-catalyst	Ligand	Solvent	Base	Yield[c]
1	CuI	-[b]	DMSO	KOH	50%
2	CuI		DMSO	KOH	71%
3	CuO nano	-	DMSO	KOH	92%
4	CuO nano	-	DMF	KOH	14%
5	CuO nano	-	DMAc	KOH	23%
6	CuO nano	-	DMSO	NaO$_t$Bu	68%
7	CuO nano	-	DMSO	NaOH	6%

[a] Reaction conditions: (4-Bromo-phenyl)-phenyl-methanone (1.0 mmol), aniline (1.0 mmol), 2.0 mmol of base in the presence of 20 mol% copper-catalyst and 40 mol% ligand in 3.0 mL solvent at 110 °C under N_2 atmosphere. [b] No ligand. [c] Isolated yield.



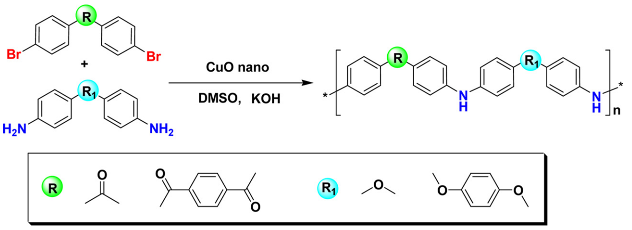
Scheme I. Proposed mechanism for CuO nanoparticles catalyzed polycondensation.



Scheme II. Synthesis of phenyl-(4-phenylamino-phenyl)-methanone.

In the exploration of a proper temperature for polymerization, we have selected combination of CuO nanoparticles, DMSO and KOH catalyst systems for the PIEK-1 (Scheme III). When increasing the temperature from 60 to 150 °C, the yields increased at first and then decreased after 110 °C. And the M_n and M_w underwent a similar process. It was implied, in Table II, that a temperature of 110 °C was more suitable for the copper-catalyzed polycondensation to produce the poly(imino eher ketone)s with relatively higher molecular weights.

With optimized conditions now in hand, we conducted the coupling reactions of aryl halides and primary aromatic diamines in the presence of CuO nanoparticles and KOH in DMSO at 110 °C under N_2 (Scheme III), and the result was summarized in Table III. We were delighted to find that the catalytic system was able to facilitate the synthesis of macromolecular. The synthesized polymers showed a considerable molecular weight and yield. The molecular weights of the polymers were measured by GPC (calibrated by polystyrene standards).



Scheme III. Synthesis of Poly(imino ether ketone)s (PIEKs).

Table II. Effect of Temperature on Molecular Weight and Yield of the Products[a]

Temperature (°C)	$M_n/10^3$	$M_w/10^3$	M_w/M_n	Yeild (%)
80	-[b]	-	-	<10
90	2.12	6.27	2.96	76
100	3.76	9.90	2.63	82
110	6.10	13.90	3.00	87
120	5.82	13.27	2.28	85
130	2.21	6.43	2.91	84
140	1.24	3.02	2.44	65
150	1.20	2.90	2.42	47

[a] Copper-catalyst: CuO nanoparticles, Solvent: DMSO, Alkali: KOH.
[b] -: No polymer formed.

Table III. The Polymer Weight and Polydispersity Index (PDI) of Poly(imino ether ketone)s

Polymer Code	M_n	M_w	M_w/M_n	Yield (%)
PIEK-1	6,100	13,900	2.28	87
PIEK-2	5,600	16,800	3.00	91
PIEK-3	3,900	13,100	3.36	94

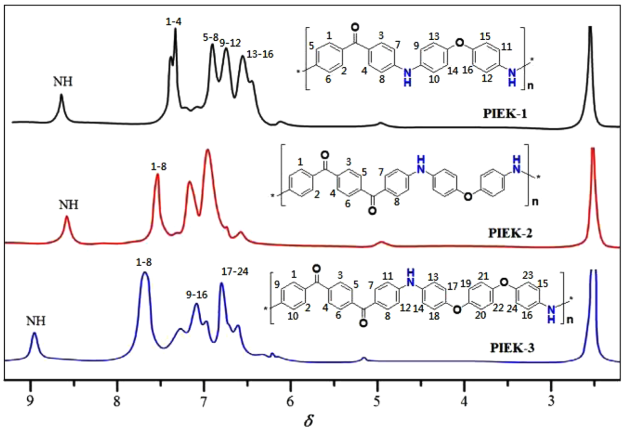


Figure 1. ^{1}H NMR spectra of Poly(imino ether ketone)s (PIEKs) in DMSO-d_6.

The synthesized polymers were characterized by FTIR, ^{1}H NMR and elemental analyses, the results of which were consistent with the proposed structures. As an example, the ^{1}H NMR spectrum of PIEKs was given in Figure 1 (DMSO-d_6). The signals of NH at around δ 8.7 ppm suggested the occurrence of the polymerization. However, we could conclude that (PIEK)s contained a low concentration of amino end groups (resonances at *ca.* 5 ppm). That might ascribe to that our molecular weight is not high enough.

Thermal Properties of PIEKs. In general, the thermal stability of the polymer plays a crucial role in determining their processing and applicability. Figure 2 showed the primary thermogravimetric curves of PIEKs. Thermal analysis (TG) curves revealed that the polymers were thermally stable and showed a single stage thermal degradation. Their temperatures for 5% weight loss were all above 400 °C, illustrating their excellent stabilities against thermal decomposition. Char yield, an easy and important measurement, is correlated to the ability to sustain combustion. For the PIEKs the char yields in nitrogen at 800 °C were up to 50%. Differential scanning calorimetry (DSC) of this three polymer up to 170 °C showed a single T_g (the inset in Figure 2). The absence of a melting temperature suggested corresponding amorphous polymer structures. All polymers displayed high T_gs ranging from 175 to 220 °C. The T_gs was higher than those of the related poly(ether ketone)s (PEKs) which range from 129 to 167 °C. The good thermal behavior of the PIEK polymers suggested that they could be considered as a new class of high performance polymers.

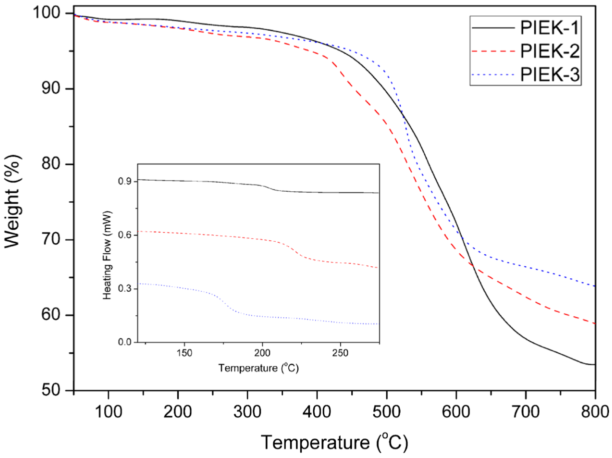


Figure 2. TG and DSC curves of Poly(imino ether ketone)s (PIEKs).

Preparation of PIEK Foam. Low density PIEK foam with open net structure required a solvent able to dissolve PIEK at high temperature and partially or not dissolved at low temperature, during the preparing process. The solubility behavior of the polymer in common organic solvents was listed in Table IV. Compared the listed solvents in Table IV, 1,4-dioxane and $CHCl_3$ were the suitable solvents for preparing low PIEK foam. In this paper, we planned to realize preparation of

Table IV. Solubility of Poly(imino ether ketone)s (PIEKs)[a]

Polymer Code	DMAc	DMSO	DMF	1,4-dioxane	$CHCl_3$
PIEK-1	+ +	+ +	+ +	+ -	+ -
PIEK-2	+ +	+ +	+ +	--	+ -
PIEK-3	+ +	+ +	+ +	--	+ +

[a] The solubility behavior was qualitatively determined by the dissolution of 50 mg of solid polymers in 1 mL of organic solvents at room temperature and 60 °C. ++: Solid polymer was completely dissolved at room temperature. +-: Solid polymer was completely dissolved at 60 °C. --: Solid polymer could swell at 60 °C.

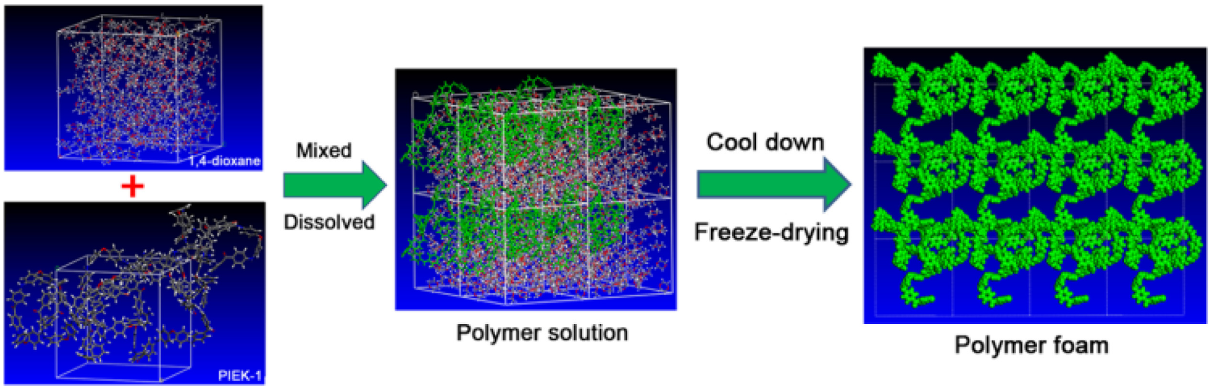


Figure 3. Preparation process of PIEK-1 foams.

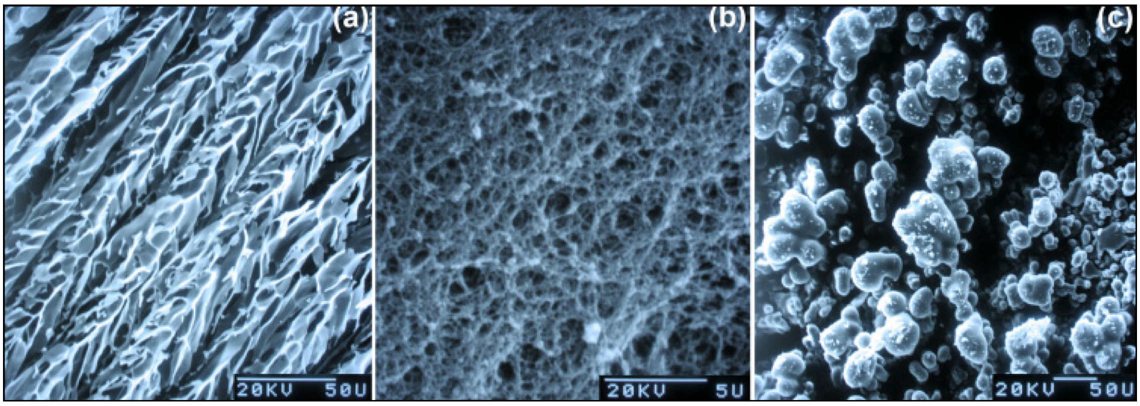


Figure 4. SEM images of PIEK-1 foams with different densities.

PIEK foam through the solution thermally induced phase separation (TIPS) and freeze-drying technology, which needed a solvent easy to sublime with a high freezing point. Hence, 1,4-dioxane was a good choice.

The preparation process of foam was shown in Figure 3. After the forming of a homogeneous solution of PIEK-1 and 1, 4-dioxane at 70 ºC, the mixture was cooled to *ca*. -190 ºC with fast cooling rate of 100 K/min. The PIEK-1 foams were successfully prepared *via* the thermally induced phase separation and the freeze-drying technology. The morphologies of PIEK-1 foams with different densities could be observed by scanning electron microscopy (SEM), from which it was discovered that the intriguing aesthetic structures of PIEK-1 foams could be obtained by changing the densities (Figure 3). With a concentration of 0.1 g/mL, the micrograph of PIEK-1 foam with the density of 96 mg/cm^3 showed the formation of cross porous net structure (Figure 4(b)). While above 0.1 g/mL, the porous gradually shrinked with increasing densities (Figure 4(a)); When below 0.1 g/mL, there was no pore structure observed (Figure 4(c)). These observations hinted that the morphologies of PIEK-1 foams were strongly dependent on concentrations of the solutions.

Thermal and Mechanical Properties of PIEK-1 Foam. The thermal property is an important factor for foam materials.

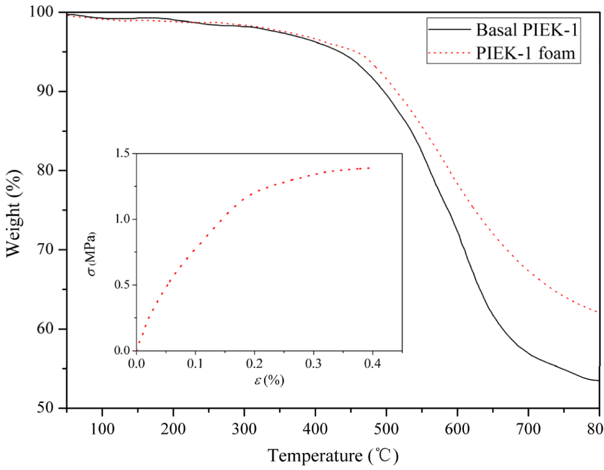


Figure 5. The TG and stress-strain curves of basal PIEK-1 and PIEK-1 foam (density of 96 mg/cm^3).

Figure 5 showed the TG curves of basal PIEK-1 and PIEK-1 foam (density: 96 mg/cm^3). Basal PIEK-1 and PIEK-1 foam exhibited the similar initial decomposition temperature (ca. 400 ºC). Whereas, the 5% decomposition temperature of PIEK-1 foam was around 465 ºC, which was a little higher than that of the basal PIEK-1 (*ca*. 440 ºC). The results suggested that the thermal decomposition behavior of the foam was delayed compared with that of the basal material, which might be attributed to the lower thermal conductivity in the foam. In addition, both basal PIEK-1 and PIEK-1 foam possessed high char yield in nitrogen at 800 ºC, with PIEK-1 foam displayed an increased char yield up to 62%, as the existence of porous structure led to a lower thermal conductivity and higher heat accumulation capacity.

Mechanical property is one of the most basic performance of polymer foam. It determines the application of the foam in the actual situation. We expect that the imino and carbonyl groups in PIEK-1 foam would result in intermolecular hydrogen bonds between polymer chains (Figure 6(b)), which may lead to good mechanical properties of the foam. In our work, hydrogen-bonding interaction of PIEK-1 foam was studied by FTIR spectroscopy. Typical FTIR spectra of PIEK-1 foam at different temperatures was shown in Figure 6(a). At room temperature the characteristic absorptions for imino groups γ(NH) appeared at 3377 cm^{-1}. This lower absorption frequency clearly indicates that N-H···O=C interaction was formed between neighboring PIEK-1 molecules. Furthermore, when the temperature rose to 200 ºC, the characteristic absorptions for imino group γ(NH) moved to 3440 cm^{-1}, which may be caused by the gradually disappearing of the intermolecular hydrogen bonds. In this work, we carried out tensile strength on PIEK-1 foam (density: 96 mg/cm^3) at room temperature. As displayed in Figure 5 (inset in Figure 5), the PIEK-1 foam showed good mechanical properties with the tensile strength of 1.37 MPa and elongation at break of 41%, which are essential requirements for high-performance polymer foams.

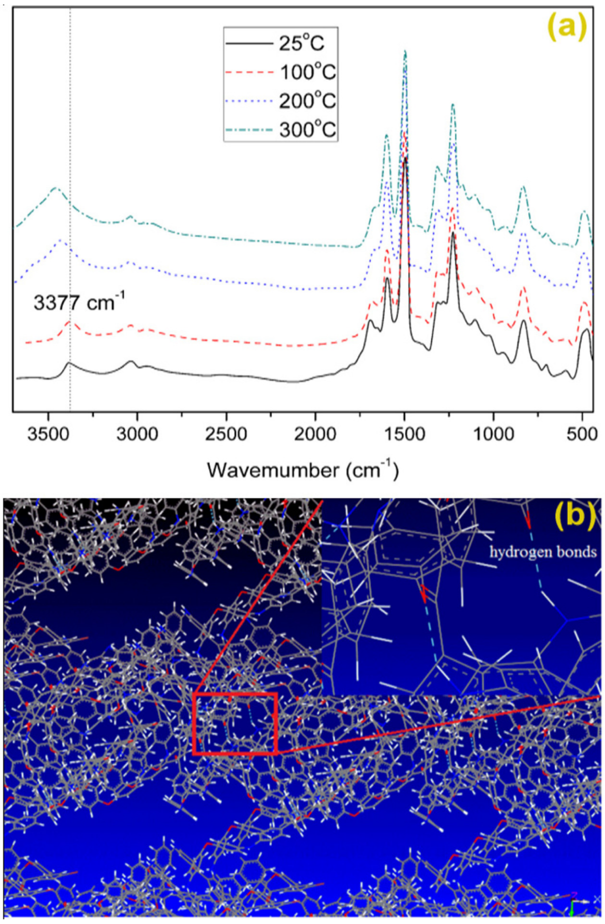


Figure 6. Hydrogen bonds between the polymer chains of PIEK-1 foam (density of 96 mg/cm^3), (a) FTIR spectra at different temperatures of PIEK-1 foam; (b) Intermolecular hydrogen bonds between H of the NH and O of the PIEK-1 polymer chains.

Conclusions

Soluble poly(imino ether ketone)s (PIEKs) with high glass transition temperatures have been obtained by a copper-catalyzed polycondensation of aromatic dibromides and aromatic ether amines. Various PIEKs were synthesized by using different monomers. As one major advantage, the combination of CuO nanoparticles and KOH, which is cheaper than the expensive palladium-catalysts, was used as an efficient catalyst for the synthesis of PIEKs. Also, the polycondensation can be carried out under a mild and efficient condition (110 ºC). Due to the good thermal stability and solubility, the PIEK-1 foam with low density, 96 mg/cm^3, has been prepared *via* thermal induced phase separation and freeze-drying technology. All these expectations are confirmed by initial mechanical and TGA measurements, indicating their potential application as a new class of high-performance polymers with a good mechanical behavior and high thermal stability.

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