

# Electrospinning of Solvent-Resistant Nanofibers Based on Poly(acrylonitrile-co-glycidyl methacrylate)

Tianhe Dai,<sup>1</sup> Katrin Ebert<sup>2</sup>

<sup>1</sup>Institute of Polymer Research, GKSS-Forschungszentrum Geesthacht GmbH, Max-Planck-Str.1, 21502 Geesthacht, Germany

<sup>2</sup>Institute of Materials Research, GKSS-Forschungszentrum Geesthacht GmbH, Max-Planck-Str.1, 21502 Geesthacht, Germany

Received 25 February 2010; accepted 11 June 2010

DOI 10.1002/app.34748

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** This article reports on the preparation of novel solvent-resistant nanofibers by electrospinning of poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) and subsequent chemical crosslinking. PANGMA nanofibers with diameters ranging from 200 to 600 nm were generated by electrospinning different solutions of PANGMA dissolved in *N,N*-dimethylformamide. Different additives were added to reduce the fiber diameter and improve the morphology of the nanofibers. The as-spun PANGMA nanofibers were crosslinked with 27 wt % aqueous ammonia solution at 50°C for 3 h to gain the solvent resistance. Swelling tests indicated that the crosslinked nanofibers swelled in several solvents but were not dissolved. The

weight loss of all the crosslinked nanofibrous mats immersed in solvents for more than 72 h was very low. The characterization by electron microscopy revealed that the nanofibrous mats maintained their structure. This was also confirmed by the results of the pore size measurements. These novel nanofibers are considered to have a great potential as supports for the immobilization of homogeneous catalysts and enzymes. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** electrospinning; crosslinking; solvent resistance; poly(acrylonitrile-co-glycidyl methacrylate); PANGMA

## INTRODUCTION

Electrospinning has drawn widespread attention in recent years due to its distinguished versatility and simplicity in fabricating nanofibrous materials.<sup>1–3</sup> Electrospun nanofibers are very promising as supports for the immobilization of homogeneous catalysts or enzymes because of their exceptionally long length, uniform diameter, huge surface area, and highly porous structure.<sup>4–6</sup>

Since most of the catalytic reactions are performed in organic solvents and at elevated temperatures, solvent- and temperature-resistant nanofibrous mats are required.<sup>7–9</sup> The majority of available electrospun nanofibers do not fulfill these requirements. One possibility to overcome this drawback is the chemical crosslinking of the polymer rendering the fibers solvent and temperature resistant.<sup>10–12</sup>

Poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) is a copolymer composed of acrylonitrile and glycidyl methacrylate (GMA). It was developed for autoclavable porous membranes serving as support for covalently immobilized enzymes.<sup>13</sup> The epoxy

group on its GMA segment offers the opportunity for the employment of PANGMA on a variety of activation/coupling chemistries for both crosslinking of nanofibers and chemical grafting of catalysts or enzymes. An effectual chemical grafting of catalysts on the support not only can greatly lower the leaching but also can make the efficient reuse and recycling of the catalysts come to reality.<sup>13,14</sup>

In this article, we describe the first results for a novel solvent-resistant electrospun nanofibrous mat, which can be obtained from PANGMA in two steps: (1) electrospinning PANGMA/DMF solution and (2) chemically crosslinking via ammonolysis. The new nanofibrous mats can be considered promising for potential applications as supports for the covalent immobilization of homogeneous catalysts and enzymes.

## EXPERIMENTAL

### Materials

PANGMA was synthesized at Evonik-Degussa AG with a molecular weight ( $M_n$ ) of  $\sim 100,000$  and GMA content of 7 mol %.<sup>13</sup> Ammonium hydroxide solution (27 wt %) was purchased from Fluka and Co. Citric acid and triethylbenzylammonium chloride (TEBAC) were purchased from  $\zeta$ -Aldrich and Co. *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc),

Correspondence to: K. Ebert (katrin.ebert@gkss.de).

dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and toluene were purchased from Merck KGaA. All chemicals were directly used without further purification.

### Preparation of PANGMA nanofibers via electrospinning

PANGMA was dissolved in DMF at room temperature with moderate stirring for 48 h to form a homogeneous solution. The polymer concentration was varied between 16 and 24 wt %. The solution was placed in a 5 mL glass syringe with a metal needle with the inner diameter of 0.8 mm. A high voltage generator was connected to the middle of the needle. A rectangular counter electrode covered with the aluminum foil was used as the collector. Electrospinning was performed at a voltage of 25 kV and a spinning distance of 25 cm. The feed rate of the solution was controlled by a syringe pump (HARVARD PHD 4400, Harvard Apparatus.Co) to be maintained at 1.5 mL/h and the electrospinning time was usually 4 h to obtain mats of sufficient thickness. After electrospinning, the nanofibrous mats were detached and washed with methanol to remove the DMF and impurities. Subsequently, the nanofibrous mats were dried under vacuum at 50°C for 24 h to remove residual solvents.

### Crosslinking of the as-spun nanofibers with ammonia

After washing with water, the PANGMA electrospun nanomats (PANGMA-ENM) were crosslinked with 27 wt % ammonium hydroxide solution. The reaction was performed at 50°C for different time intervals. Finally, the nanomats were carefully washed with water again and dried under vacuum at 50°C for 24 h.

### Characterizations

The solvent resistance of crosslinked PANGMA-ENM was tested by immersing them in different solvents (toluene, THF, DMF, DMAc and DMSO). For the swelling experiments, the nanofibrous mats were cut into pieces of 4 cm × 4 cm. Then, the weight of the dry nanomats was taken ( $W_0$ ). The samples were then immersed for 72 h in the respective solvent at room temperature and finally the weight of the thus treated sample was determined ( $W_1$ ). Subsequently, the samples were washed with methanol and dried as described before. The weight of the dried samples is referred to as  $W_2$ . The swelling rate ( $S$ ) and the weight loss rate (WL) were calculated by the following equations:

$$S = W_1/W_2 \quad (1)$$

$$WL = (W_0 - W_2)/W_0 \times 100\% \quad (2)$$

The experiments were performed with five pieces of the respective samples. The data given in the article are the average values of these five experiments.

The structures of both the uncrosslinked and crosslinked PANGMA-ENM were characterized by Attenuated Total Reflection Fourier transform infrared spectroscopy (ATR-FTIR) with a FTIR spectrophotometer (Bruker Equinox 55, Bruker Optics) in the mid-infrared range from 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$ .

The morphology of the PANGMA ENM was observed with a scanning electron microscope (LEO Gemini 1550 VP, Zeiss) at 10 kV accelerating voltage after sputter coating with gold. The average diameters of the nanofibers were calculated from 10 different single values randomly by the internal software of the SEM.

The thermal properties of crosslinked and uncrosslinked PANGMA nanofibers were studied by differential scanning calorimetry (DSC) with a Netzsch DSC 204 Phoenix<sup>®</sup> using indium standards. The glass transition temperature ( $T_g$ ) was determined by means of a dynamic scan at 10°C/min from 20 to 200°C.

The interfiber pore size of the PANGMA-ENM was determined with the liquid–gas displacement method. It is based on the measurement of pressure necessary to blow a gas through a liquid-filled membrane pore. The relationship between the pore size and the corresponding pressure is given by the Young-Laplace equation:

$$R = 2\gamma \cos \theta / \Delta P \quad (3)$$

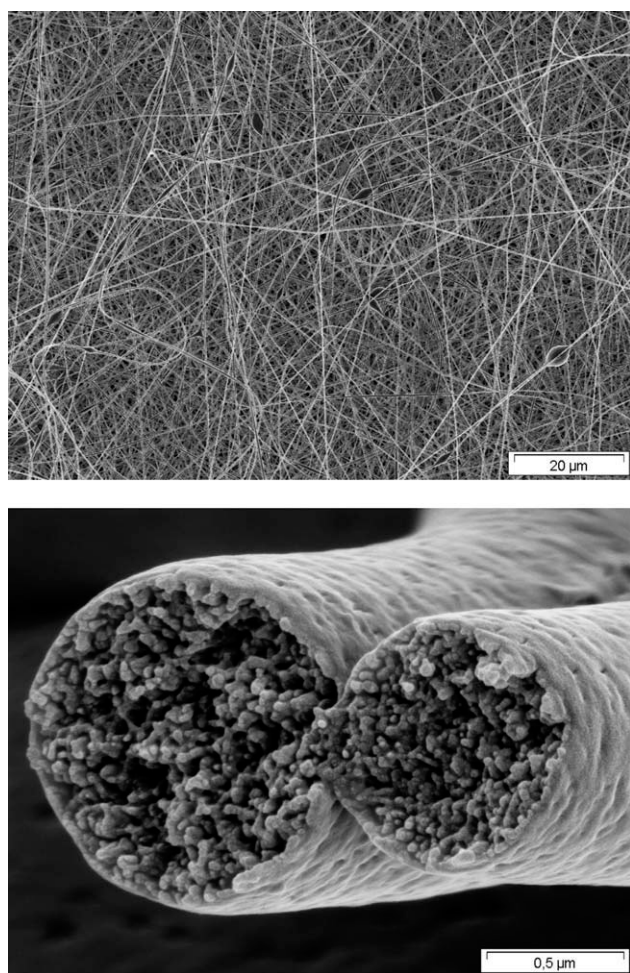
where  $R$  is radius of the pore (m),  $\Delta P$  is the differential gas pressure,  $\gamma$  is the surface tension of wetting liquid (J/m), and  $\theta$  is the contact angle.<sup>15,16</sup>

The measurements were performed with a Porometer 4.900 from Porous Materials Inc. (PMI). The PANGMA-ENM stamps with a diameter of 3 cm were immersed in the wetting fluid Porewick<sup>®</sup> from PMI (surface tension =  $16 \times 10^{-7}$  J/m = 16 dyn/cm) for more than 15 min and then placed in the test cell. By an automated procedure, a successively increasing pressure was applied across the membrane sample using nitrogen as pressurizing gas. At a certain pressure, the surface tension of the pore filling liquid in the largest pores is exceeded. The liquid is displaced and the gas flow through the open pore is monitored. By further pressure increase the liquid in the smaller pores is displaced until all pores are open. Based on the flux data through the membrane, the pore size distribution is calculated by the internal PMI software.

## RESULTS AND DISCUSSION

### Electrospinning of PANGMA nanofibers

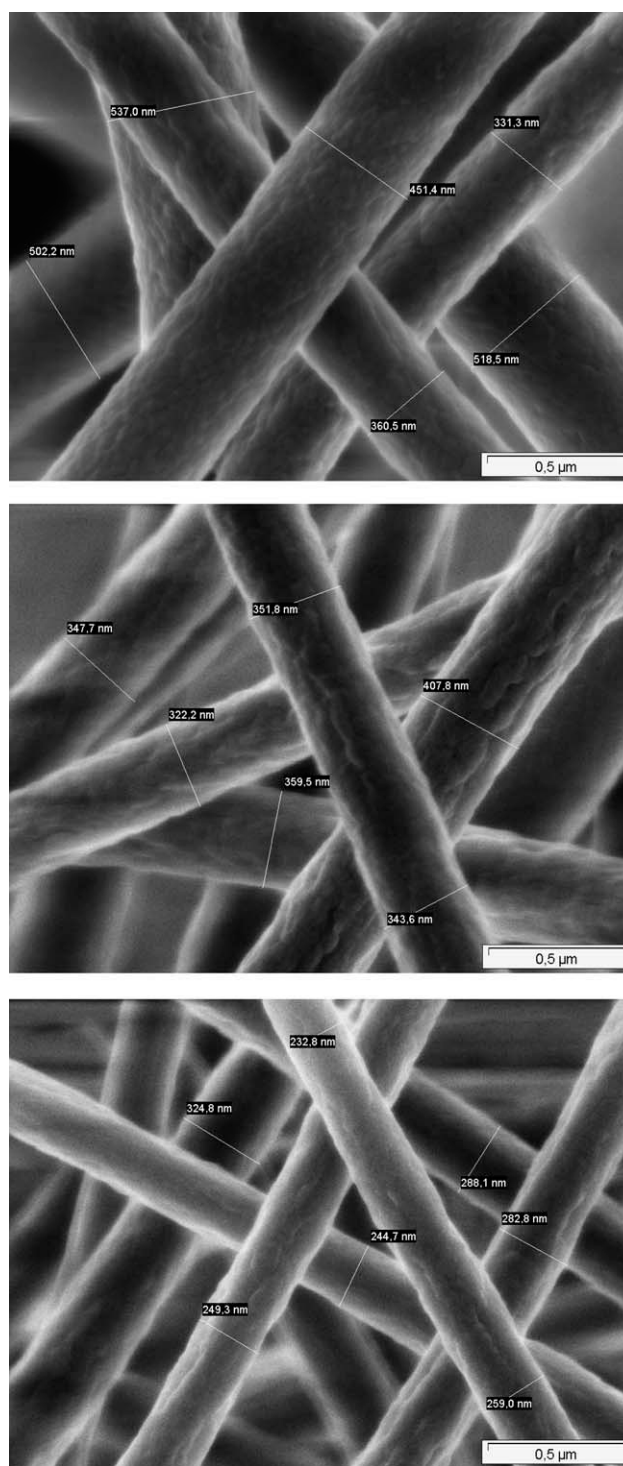
PANGMA/DMF solutions with polymer concentrations of 16 to 24 wt % were electrospun. For sake of



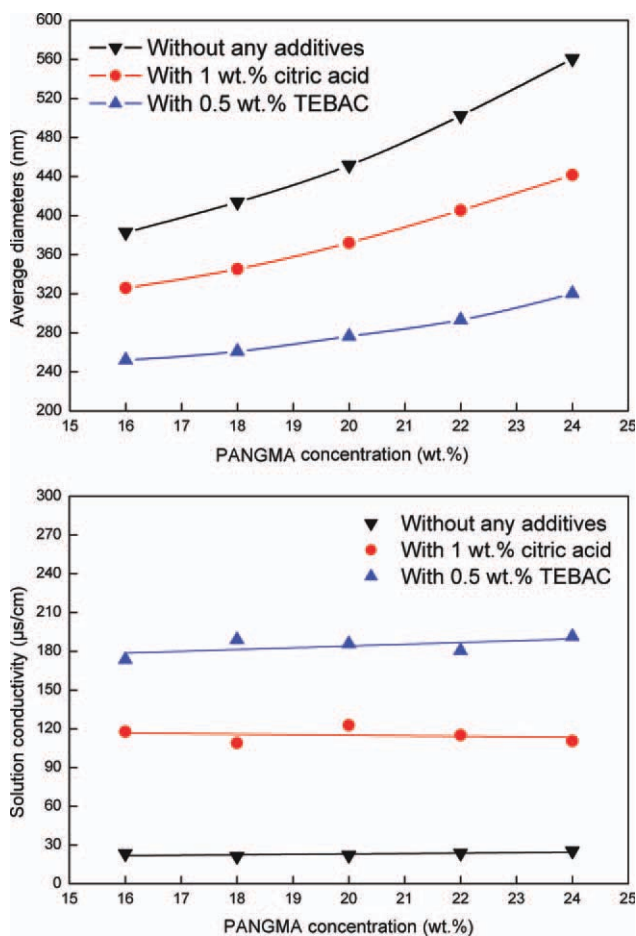
**Figure 1** SEM micrographs of PANGMA electrospun nanofibers (PANGMA concentration = 22 wt %): (a) structure of nanofibrous mat and (b) inside structure of single nanofiber.

clarity only the morphologies of the obtained nanofibers obtained from a 22 wt % solution are shown in Figure 1. (This PANGMA concentration was chosen for further experiments because of good uniformity of the electrospun fibers. The results obtained with other polymer concentrations are not included.) The nanofibrous mats have a uniform fiber size distribution practically free of beads [Fig. 1(a)]. It is obvious that the inside structure of these nanofibers seems to be nodular [Fig. 1(b)]. A possible reason for forming this structure is the phase inversion induced by inflow of methanol during the drying process of the nanofibers after electrospinning.<sup>17–19</sup> Since DMF is a low volatile solvent at room temperature (vapor pressure: 490 Pa at 25°C), it can not evaporate completely during the electrospinning process and the residual DMF will spontaneously form some solvent rich regions inside the nanofibers. After the remaining DMF diffuses out of the fibers, the original solvent rich regions transform into small pores and then such nodular structure might form.

The diameter and the morphology of the PANGMA nanofibers could be further controlled by adding citric acid or triethylbenzylammonium chloride (TEBAC) to the spinning solution. Figure 2 shows



**Figure 2** SEM micrographs of PANGMA nanofibers (PANGMA concentration = 22 wt %): (a) without any additives, (b) with 1 wt % citric acid, and (c) with 0.5 wt % TEBAC, the concentration of spinning solution is 22 wt %.



**Figure 3** Influence of (a) PANGMA concentration and additives on average diameter of electrospun nanofibers; (b) PANGMA concentration and additives on electrical conductivity of the spinning solutions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the SEM photographs of the nanofibers electrospun from solution containing 1 wt % citric acid [Fig. 2(b)], 0.5 wt % TEBAC [Fig. 2(c)], and without any additives [Fig. 2(a)]. The diameters of the neat PANGMA nanofibers are in the range of 400 to 600 nm. With the additive containing spinning solutions the thicknesses are reduced to 250 to 350 nm [Fig. 3(a)].

In a number of references it is reported that additives can influence the diameters of nanofibers by altering the conductivity of the spinning solution.<sup>20,21</sup> Generally, the electrical conductivity of a solution reflects a charge density on a jet, which will have big influence on the elongation level of the jet by the electrical force. Therefore, under the same applied voltage and spinning distance, a solution with a higher electrical conductivity may cause higher elongation of a jet along its axis. As a consequence, electrospun nanofibers with smaller diameters are obtained. Experiments were performed to study the relationship between fiber diameters and

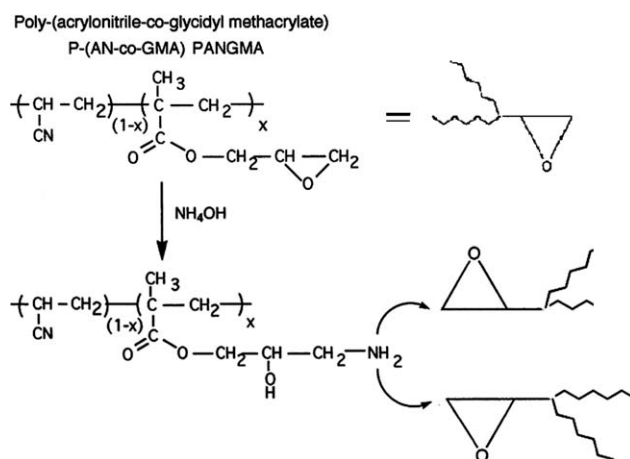
composition of the spinning solution conductivity for the PANGMA/DMF system.

Figure 3(a) shows the average diameter of the PANGMA nanofibers with and without adding additives and Figure 3(b) shows the solution conductivity before and after adding additives. It can be clearly seen that the solution conductivity increases, whereas the average fiber diameter decreases after the additives are added. As mentioned above, nanofibers with thinner diameters can be obtained from the spinning solution with higher solution conductivity. A small amount of additives may change the solution conductivity significantly and thus reduce the diameters of the nanofibers.

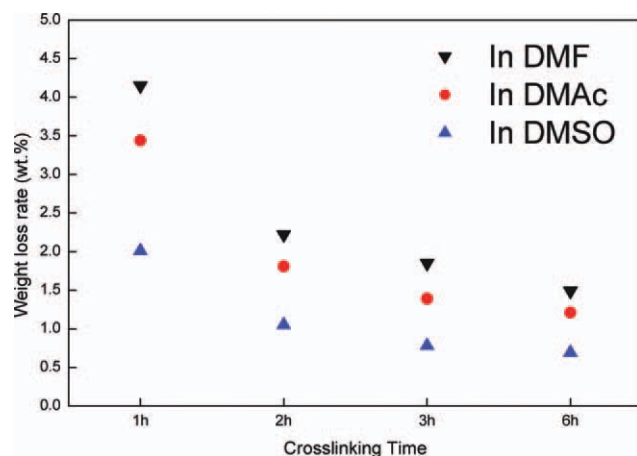
### Crosslinking and solvent-resistance measurements

Crosslinking of the as-spun PANGMA nanofibers is required to gain the resistance in organic solvents, such as DMF and DMSO. Ammonia was chosen as the crosslinking agent for the as-spun PANGMA nanofibers. The proposed route for the crosslinking reaction is shown in Scheme 1. The reaction route is described by Hicke et al.<sup>13</sup> Briefly, during the reaction with ammonia, primary amino groups are formed by the conversion of epoxy groups. As the reaction proceeds further, epoxy groups may react with the already formed amino groups. The crosslinking reaction was performed at 50°C and different crosslinking time to obtain the best crosslinking conditions. The solvent resistance of crosslinked PANGMA-ENM was characterized by determining the weight loss rate of the ENM after immersion in the respective solvent for 72 h.

In Figure 4, the weight loss rate of PANGMA-ENM dependent on the crosslinking time is given. The weight loss rate at comparable crosslinking times decreases in the order DMF, DMAc, and DMSO. Correspondingly, the same trend was



**Scheme 1** Crosslinking reaction route of the as-spun PANGMA nanofibers.<sup>13</sup>



**Figure 4** Weight loss of PANGMA-ENM dependent on the crosslinking time after immersion in organic solvents for 72 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

observed for the swelling rates which are 17%, 8.9%, and 7.5%, respectively. Generally, the weight loss rate decreases with increasing crosslinking time for all tested solvents. After 1 h crosslinking time, the weight loss is more than 4 wt % in the case of DMF and only about 2 wt % for the samples immersed in DMSO. This decrease is moderate between 2 and 6 h. After 3 and 6 h, respectively, the weight loss is less than 2 wt % in all solvents. For further experiments, fibers crosslinked for 3 h were chosen.

FTIR measurements were performed to structurally verify the crosslinking of PANGMA nanofibers. Figure 5 shows the FTIR spectra of neat (curve (a)) and crosslinked (curve (b)) nanofibers. On curve (a), there is a clear peak near  $908\text{ cm}^{-1}$  (characteristic peak of epoxy group), which shows the existence of epoxy groups in neat PANGMA nanofibers. Meanwhile, no obvious peak near  $908\text{ cm}^{-1}$  can be found in the spectrum (b), which further proves that epoxy groups in PANGMA have been crosslinked by ammonia.

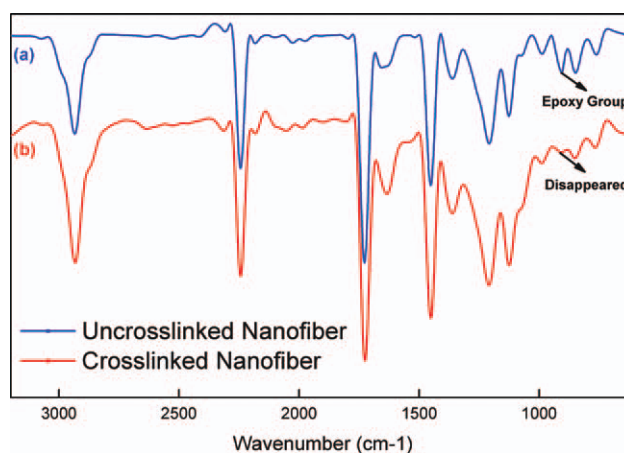
Figure 6 shows the SEM photos of the crosslinked PANGMA nanofibers after immersion in organic solvents for 72 h at room temperature. For comparison the crosslinked nanofibers without being immersed in any solvent are included in Figure 6(a). It can be seen that the fibers are rather unaffected in the case of THF, toluene, and DMSO [Fig. 6(b–d)]. Since PANGMA has only limited (DMSO) or even no solubility (THF, toluene) in these solvents, this is not surprising. In DMAc and DMF, a higher swelling of the PANGMA nanofibers was observed as it was discussed before. Correspondingly, the shape of the fibers is changed [Fig. 6(e,f)] in comparison to the untreated fibers [Fig. 6(a)]. Obviously, the nanofibers become more ribbon like, especially in the case of DMF-treated

fibers [Fig. 6(f)]. Generally, the structure of the nanomats is kept, although it seems that nanomats which have been immersed in DMF have a more densified interfiber structure. However, the results show that the crosslinked PANGMA-ENM have superior solvent resistance in a series of organic solvents and therefore are suitable for the applications in such environments.

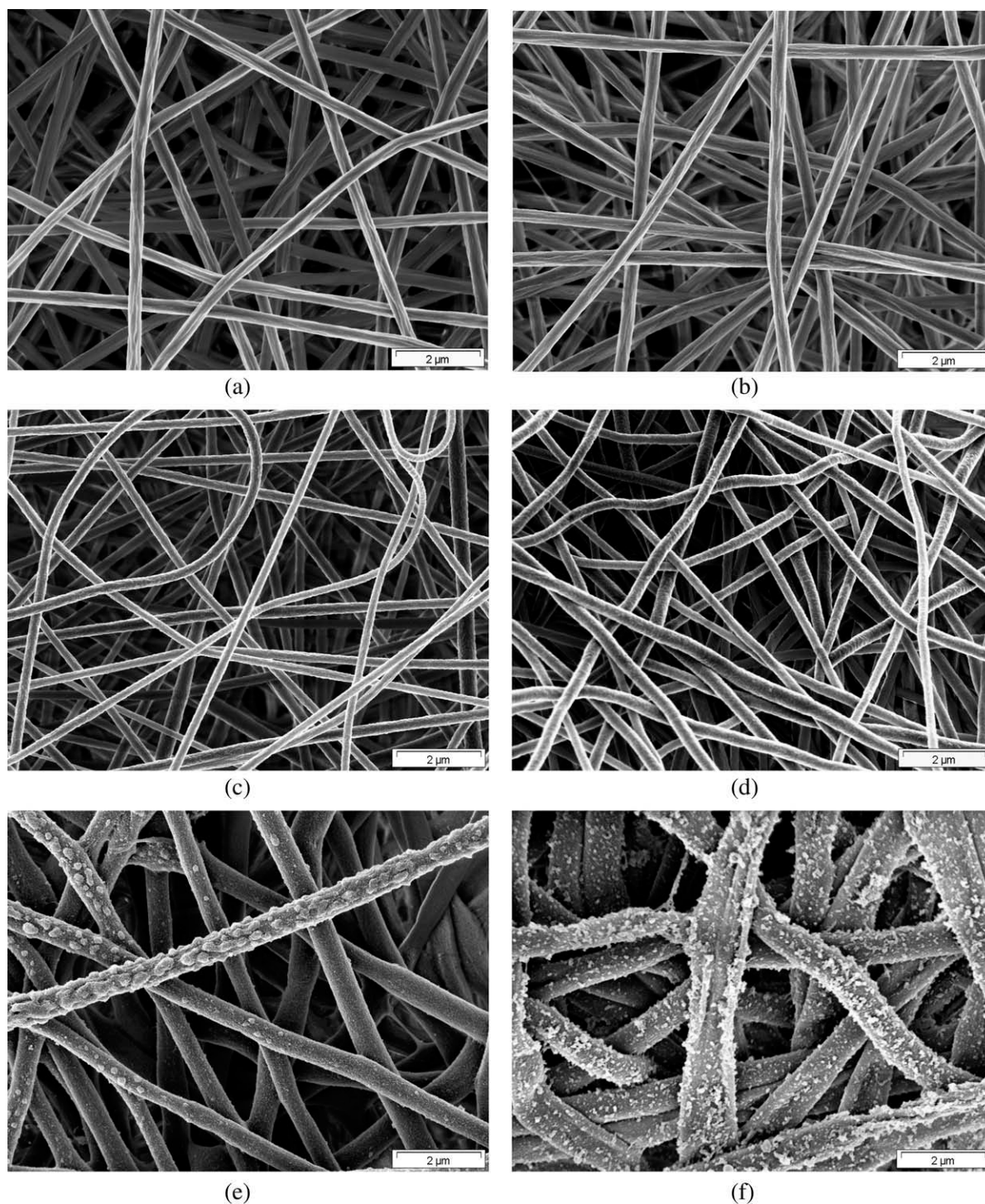
It is noteworthy that PANGMA nanofibers with only 7 mol % GMA content already have enough epoxy groups to obtain this excellent solvent resistance. It is feasible to synthesize PANGMA with a higher GMA content (higher than 15 mol %) and partially crosslink them after electrospinning to keep enough epoxy groups for the additional binding capacity for covalent immobilization of ligands of homogeneous catalysts. Moreover, the formed amino groups during the crosslinking can also be used for the covalent immobilization of enzymes on the PANGMA nanofibers.

#### Thermal stability of PANGMA nanofibers

Crosslinking also improved the thermal stability of the PANGMA nanofibers. Figure 7 shows the DSC thermograms for crosslinked and uncrosslinked PANGMA nanofibers. After 3 h crosslinking, the glass transition temperature ( $T_g$ ) of the nanofibers increases from  $98.7$  to  $109^\circ\text{C}$ , and then further increases with increase in crosslinking time to almost  $130^\circ\text{C}$  after 48 h. This is due to the decreasing flexibility of polymer chains as a result of the formation of a crosslinked network. As a consequence, the glass transition temperature increases. These results and analysis indicate that PANGMA nanofibers still have big potential for further improvement of thermal stability. More experiments



**Figure 5** FTIR spectrum of PANGMA nanofibers: (a) before and (b) after crosslinking, crosslinked samples prepared with ammonolysis at  $50^\circ\text{C}$  for 3 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** SEM micrographs of crosslinked PANGMA nanofibers: (a) before, and after immersion in different solvents at room temperature for 72 h: (b) THF; (c) Toluene; (d) DMSO; (e) DMAc; and (f) DMF.

have been carried out to deeply understand the relationship between crosslinking and thermal property of PANGMA nanofibers.

#### Pore size distribution of PANGMA-ENMs

In Figure 8, the pore size distribution of uncrosslinked, crosslinked, and solvent-treated PANGMA-

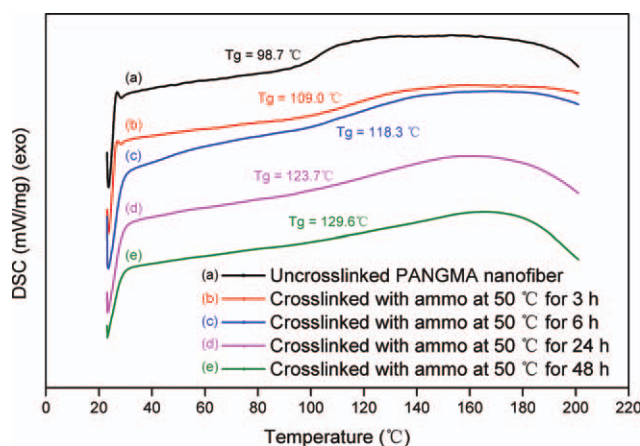
ENM are shown. For all studied nanomats, pore sizes ranging from 0.6 to 2.8 μm were determined. The maximum frequency of pores for uncrosslinked and crosslinked nanomats was found at 1.4 μm. This maximum is shifted to about 1 μm for crosslinked nanomats which have been stored in DMF for 72 h at room temperature. The results correspond to those obtained from the SEM studies. After the

treatment with DMF, the nanofibers changed their shape to ribbons thereby decreasing the interfiber distances and consequently, resulting in lower interfiber pore sizes.

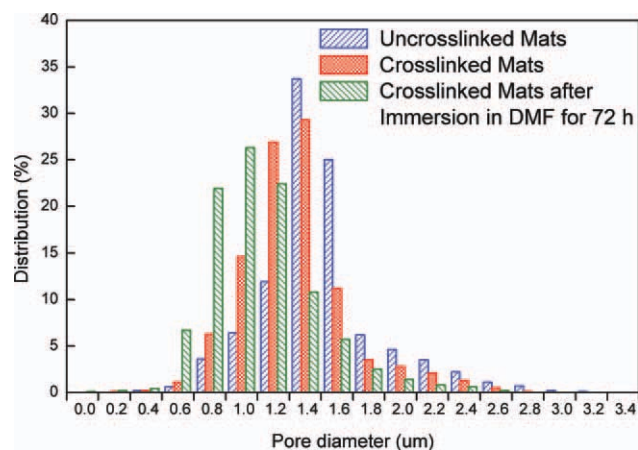
Furthermore, it may be speculated whether a crosslinking temperature of 50°C might induce a slight shrinkage of nanomats due to relaxations of frozen-in local stresses in the nanofibers. For the reduction after immersion in DMF, the swelling of the crosslinked nanomats will alter both the shape of nanofibers and the structure of the nanomats. The growth of the nanofibers caused by swelling will occupy part of the pore space, resulting in the reduction of pore size, and the shrinking of nanomats during the drying process after swelling will reduce the pore size too.

## CONCLUSIONS

We have demonstrated the preparation of a novel solvent-resistant nanofiber based on the electrospinning of PANGMA and the subsequent crosslinking of the nanofibers. Results of relative characterizations indicate that the diameter of the PANGMA nanofibers is in the range of 200 to 600 nm and can be controlled by adding different additives into the electrospinning solution. The as-spun PANGMA nanofibers can be successfully crosslinked by 27 wt % ammonia aqueous solution at 50°C for 3 h. The pore size of the PANGMA-ENM will reduce after crosslinking and immersion into the solvents. The crosslinked PANGMA nanofibers show a good resistance against most of the solvents which are commonly used in catalytic reactions. Thus, they have potential applications in the immobilization of homogeneous catalysts and enzymes.



**Figure 7** DSC curves of un- and crosslinked PANGMA nanofibers: (a) uncrosslinked; (b) crosslinking time = 3 h; (c) crosslinking time = 6 h; (d) crosslinking time = 24 h; and (e) crosslinking time = 48 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8** Pore size distribution of the neat and crosslinked PANGMA-ENM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

This work was financially supported by a DAAD-HGF fellowship for Tianhe Dai, who also thanks Prof. Volker Abetz for helpful discussions. The authors thank Karen-Marita Prause and Sabrina Bolmer for the SEM measurements.

## References

- Dzenis, Y. *Science* 2004, 304, 1917.
- Dersch, R.; Steinhart, M.; Boudriot, U.; Greiner, A.; Wendorff, J. H. *Polym Adv Technol* 2005, 16, 276.
- Li, D.; Xia, Y. N. *Adv Mater* 2004, 16, 1151.
- Wang, Z. G.; Wan, L. S.; Liu, Z. M.; Huang, X. J.; Xu, Z. K. *J Mol Catal B Enzym* 2009, 56, 189.
- Barbaro, P.; Liguori, F. *Chem Rev* 2009, 109, 515.
- Wan, L. S.; Ke, B. B.; Wu, J.; Xu, Z. K. *J Phys Chem C* 2007, 111, 14091.
- McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem Rev* 2002, 102, 3275.
- Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem Rev* 2003, 103, 3401.
- Bergbreiter, D. E. *Chem Rev* 2002, 102, 3345.
- Chen, C. Z.; Wang, L.; Huang, Y. *Mater Lett* 2009, 63, 569.
- Stasiak, M.; Studer, A.; Greiner, A.; Wendorff, J. H. *Chem Eur J* 2007, 13, 6150.
- Stasiak, M.; Röben, K.; Rosenberger, N.; Schleth, F.; Studer, A.; Greiner, A.; Wendorff, J. H. *Polymer* 2007, 48, 5208.
- Hicke, H. G.; Lehmann, I.; Malsch, G.; Ulbricht, M.; Becker, M. *J Membr Sci* 2002, 198, 187.
- Lee, M. Y.; Cha, S. Y.; Park, W. H. *Polymer* 1999, 40, 3787.
- Ebert, K.; Fritsch, D.; Koll, J.; Tjahjaviguna, C. *J Membr Sci* 2004, 233, 71.
- Gopal, R.; Kaur, S.; Ma, Z. W.; Chan, C.; Ramakrishna, S.; Matsuura, T. *J Membr Sci* 2006, 281, 581.
- Sungwon, C.; Jeongrae, K.; Youngrack, A.; Seongmu, J.; Elton, J. C. *Chem Mater* 2007, 19, 104.
- Wu, Y. Q.; Clark, R. L. *J Colloid Interface Sci* 2007, 310, 529.
- Qin, Z. H.; Yu, H.; Chen, Y. M.; Zhu, M. F. *Mater Lett* 2009, 63, 415.
- Delaram, F.; Mehdi, R.; Naser, M.; Behrooz, V. *e-Polymers* 2009, 104, 1.
- Uyar, T.; Besenbacher, F. *Polymer* 2008, 49, 5336.