

Preparation of Honeycomb Films from Nitril Poly(ether ether ketone)s via Water-Droplet Templating

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ABSTRACT: The fabrication of honeycomb-patterned films from nitril poly(ether ether ketone)s (PEEK-NO₂) in a high-humidity atmosphere was reported in this article. PEEK-NO₂ was prepared through acid (nitric acid and sulfuric acid) nitration from poly(ether ether ketone)s (PEEK). The obtained polymer, which was characterized by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and differential scanning calorimetry (DSC) showed excellent solubility and thermal stability. Some influence factors on the pattern formation and the fabrication of the porous structure, such as the solution concentration, the solvent, and the atmosphere humidity, were

investigated. The results showed that with the increase of the solution concentration, the aperture of the film diminished gradually; the lower the solvent's boiling point were, the smaller the film's apertures were and the more regular the pores' arrange; only under high-humidity circumstances could obvious and ordered honeycomb films be formed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2090–2095, 2009

Key words: poly(ether ether ketone)s (PEEK); nitril poly(ether ether ketone)s (PEEK-NO₂); high humidity; honeycomb porous structure

INTRODUCTION

The formation of honeycomb films in high humidity was one of the great development in the field of molecular self-assembly,¹ and was first described by Frangois and coworkers.^{2–4} They can be applied in chemical sensors,⁵ scaffolds for catalysis,⁶ biology,⁷ tissue engineering,⁸ etc. The process of forming the honeycomb films was described as follows: (1) water droplets were condensed on the surface of the solution because of cooling by solvent evaporation; (2) because of the incompatibility of the organic solvent and water, as well as the hydrophilic/hydrophobic balance of the polymer solution, water droplets were closely packed on the surface of the solution; and (3) after the water and the solvent evaporated completely, honeycomb films were prepared. Because this method was manipulated easily, it attracted much attention.^{9–14}

As a novel semicrystalline polymer, poly(ether ether ketone)s (PEEK) has been used widely in

aerospace, microelectronics, automobile, chemical engineering, and other fields for its excellent thermal, chemical mechanical properties, and environment stabilities.^{15–18} However, it is difficult for PEEK to be used as thin films because it can hardly be dissolved in any solvents except for concentrated sulfuric acid.^{19–22} But after nitril was introduced into the molecular chain of PEEK, the solubility and thermal stability of the polymer were improved greatly.²³

In this article, PEEK-NO₂ was prepared through acid (nitric acid and sulfuric acid) nitration from PEEK. The structure and properties of PEEK-NO₂ were characterized by FT-IR, XRD, and DSC. Then, PEEK-NO₂/solvent (CH₂Cl₂/CHCl₃/CH₂ClCH₂Cl) solutions were cast on glass substrates to form honeycomb films. The influences of the solution concentration, the solvent, and the atmosphere humidity on the pattern formation and fabrication of the porous structure were investigated.

EXPERIMENTAL

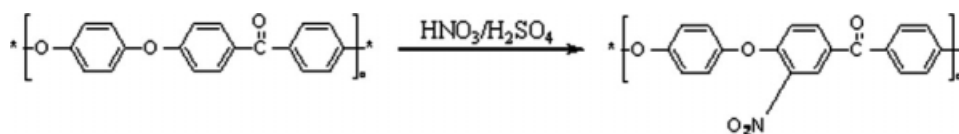
Materials

Poly(ether ether ketone)s was purchased from JiLin University and dried for 12 h at 80°C before use, sulfuric acid (98%, AR, Shanghai Lingfeng Chemical Reagent), nitric acid (65%–69%, AR, Beijing Beihua

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Scheme 1 Synthetic route for PEEK-NO₂.

Chemical Reagent), dichloromethane (AR, Beijing Chemical Reagent), chloroform (AR, Beijing Chemical Reagent), 1,2-dichloromethane (AR, Beijing Chemical Reagent).

Preparation of PEEK-NO₂

Into a 250- mL three-necked flask equipped with a mechanical stirrer, a dropping funnel and a condenser, the dried PEEK (12 g ± 0.1) and concentrated sulfuric acid (30 mL) were placed. Concentrated sulfuric acid (15 mL) and nitric acid (15 mL) were added dropwise into the stirred mixture through the dropping funnel at a rate of 20 drops per minute. After 10 h, the mixture was washed thoroughly with water, then filtered and dried. The obtained product was light yellow solid.

The chemical structure and schematic synthetic route of this polymer are shown in Scheme 1.

Film preparation

PEEK-NO₂ was dissolved in solvent (CH₂Cl₂ or CHCl₃ or CH₂ClCH₂Cl) at first. The polymer solutions were then directly cast on glass substrates at room temperature and were placed into a chamber whose relative humidity was 95%. After the solvent evaporated completely, the films were obtained.

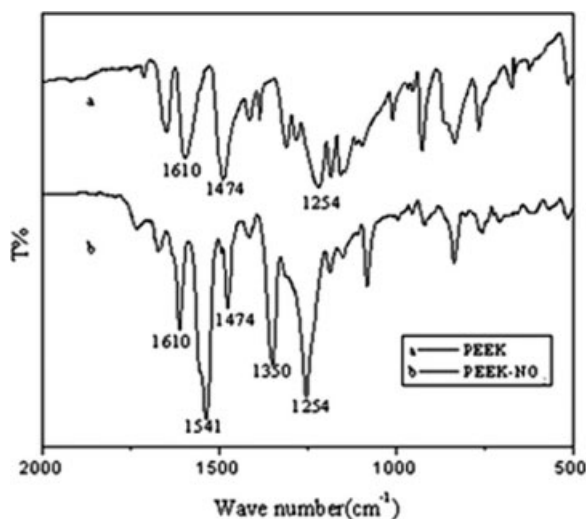


Figure 1 IR spectra of PEEK and PEEK-NO₂.

Measurements

FT-IR spectra (KBr films) were measured on a Nicolet Magna 560 Fourier transform infrared spectrometer. The glass-transition temperature (T_g) was determined by DSC (Mettler Toledo DSC 821^e) at a heating rate of 10°C/min under nitrogen. XRD was performed on an X'Pert PRO MPD instrument and the 2θ angle region between 5 and 80°C. The surface morphology of the microstructure films was observed by scanning electron microscopy (SEM) with a Hitachi s-4300 instrument at 25 kV and 10 μA.

RESULTS AND DISCUSSION

Properties of PEEK-NO₂

Figure 1 shows the FT-IR measurement for the PEEK and the PEEK-NO₂. It can be seen that the absorptions at about 1610 cm⁻¹ assigned to C=O stretching vibrations in -Ar-C(=O)-Ar-, the absorptions at about 1254 cm⁻¹ attributed to C-O stretching vibrations in -Ar-O-, and the absorptions at about 1541 cm⁻¹ and 1350 cm⁻¹ assigned to the asymmetric and symmetric stretching vibrations in -NO₂. These results indicated that -NO₂ had been introduced into PEEK successfully.

Figure 2 shows the crystallinity of PEEK and PEEK-NO₂ that were examined by XRD. It can be seen that the high and sharp diffraction apices were assigned to PEEK and the broad dispersion diffraction apex between 20 and 25°C was attributed to

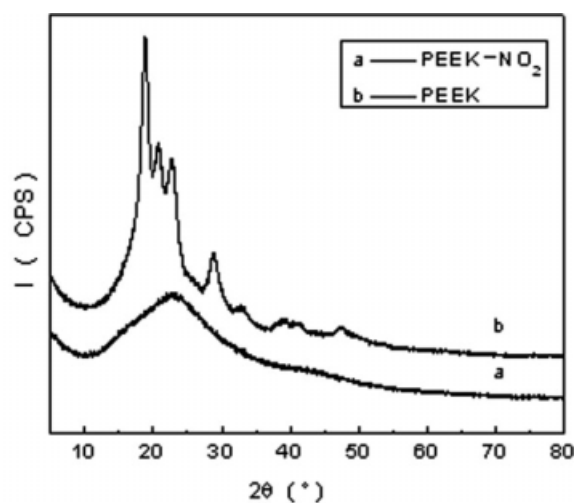


Figure 2 XRD spectra of PEEK and PEEK-NO₂.

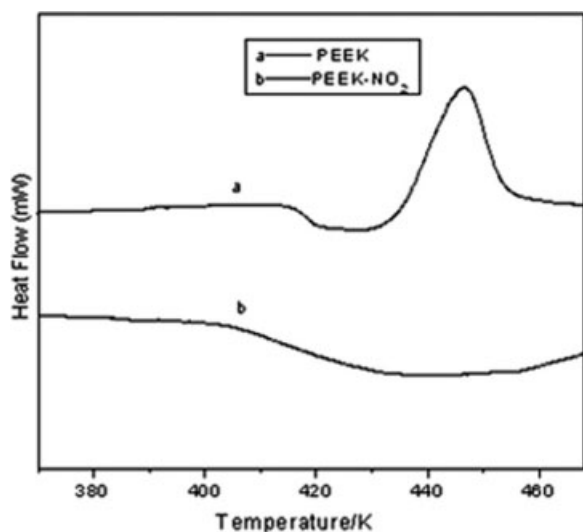


Figure 3 DSC trace of PEEK and PEEK-NO₂.

PEEK-NO₂. The results indicated that PEEK was a semicrystalline polymer and PEEK-NO₂ was an amorphous polymer with a long-range and ordered molecule chain. The reason is that the molecule chain was made relatively irregular after -NO₂ was introduced into the chain, but the total chain still kept the long-range and ordered structure, so the PEEK-NO₂ exhibited one dispersion diffraction apex.

Figure 3 shows the thermal property of PEEK and PEEK-NO₂ that were evaluated by DSC. The T_g of PEEK-NO₂ was 413 K, it was slightly low than that of the PEEK ($T_g = 416$ K). It is because the introduction of the side group (-NO₂) destroyed the order of the chain and influenced the gather of the molecules that can produce inner plasticity. The polymer turned into amorphous polymer and it needed less heat, so the T_g was a little lower.

The solubility was determined by dissolving 0.01 g of PEEK-NO₂ in 10 mL of solvent at room temperature. Table I summarizes its solubility. It can be seen that PEEK-NO₂ exhibited good solubility in common organic solvents, such as DMF, DMAC, DMSO, CHCl₃, CH₂Cl₂, CH₂ClCH₂Cl, and acetone. The

TABLE I
Solubility of the PEEK-NO₂ in Different Solvents

Solvents	PEEK-NO ₂
DMF	+
DMAC	+
DMSO	+
Acetone	+
CHCl ₃	+
CH ₂ Cl ₂	+
CH ₂ ClCH ₂ Cl	+

+ Soluble; - Insoluble

good solubility of the polymer could be interpreted by the introduction of nitril group and the bulk pendant group in the polymer backbone, which induced the decrease of the interaction of the polymer chain and destroyed the crystal of the polymer. It has been reported before that the good compatibility between the polymers and their solvents was beneficial to the formation of regular structures.^{24,25} This good solubility of PEEK-NO₂ in organic solvent provided the precondition for the formation of the regular patterns.

Formation of honeycomb structure in PEEK-NO₂ film and influence of solution concentration

Figure 4 shows the SEM images of PEEK-NO₂ films prepared from different solution concentrations. It is found that with increasing solution concentration, the apertures of the film became small and regular pore structure could not be obtained when the concentration increased to a certain degree (2 g/L). It is well known that regular pore structures can only be formed under higher humidity environment. The amount of the polymer molecule on the solution surface increased with the increase of the solution concentration, so the film surface became thicker and the surface tension increased, then the water droplets could not immerse into the polymer solution, and the humidity environment was not enough to form regular pore structures. Moreover, the viscosity of the polymer solution, which increased with the

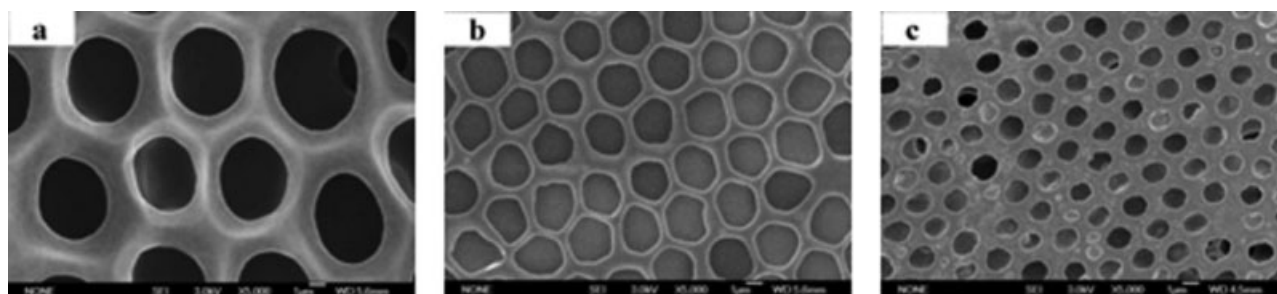


Figure 4 SEM images of porous structure in PEEK-NO₂ films prepared from different solution concentrations. (a) 0.5 g/L; (b) 1 g/L; (c) 2 g/L. Other conditions: temperature: 25°C; relative humidity: 95%; spreading volume: 100 μ L.

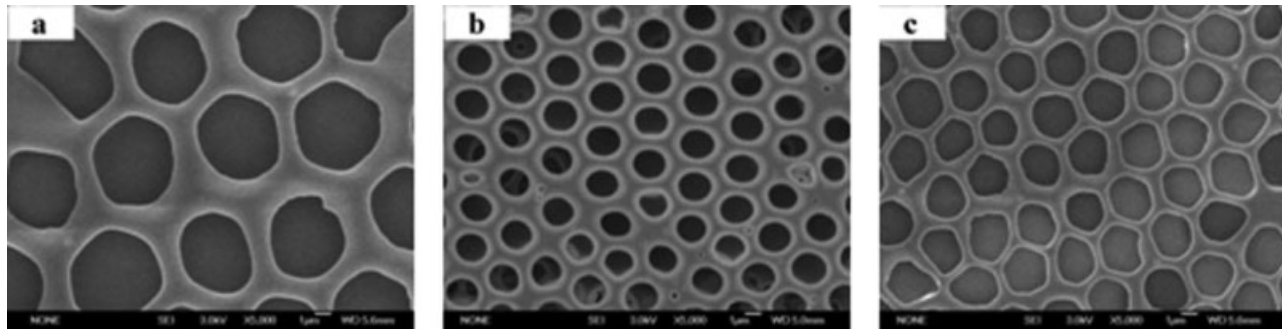


Figure 5 SEM images of porous structure in PEEK-NO₂ films prepared from different solvents. (a) CH₂ClCH₂Cl; (b) CH₂Cl₂; (c) CHCl₃. Other conditions: temperature: 25°C; relative humidity: 95%; concentration: 1 g/L; spreading volume: 100 μL.

increase of the concentration, also prevented the growth of the water droplets on the solution surface and resulted in the aperture diminishing.

Influence of solvent to the formation of regular pore structure

Figure 5 shows the SEM images of PEEK-NO₂ prepared in different solvents (CH₂Cl₂, CHCl₃, and

CH₂ClCH₂Cl). It is found that regular pore structures can be formed in these solvents, but the pore size of the films became larger with increasing boiling point of the solvents (CH₂Cl₂ < CHCl₃ < CH₂ClCH₂Cl). That is because the high boiling point solvent needed more time to evaporate completely, then the water droplets had more time to assemble and grow on the solution surface, and consequently the larger pores were formed.

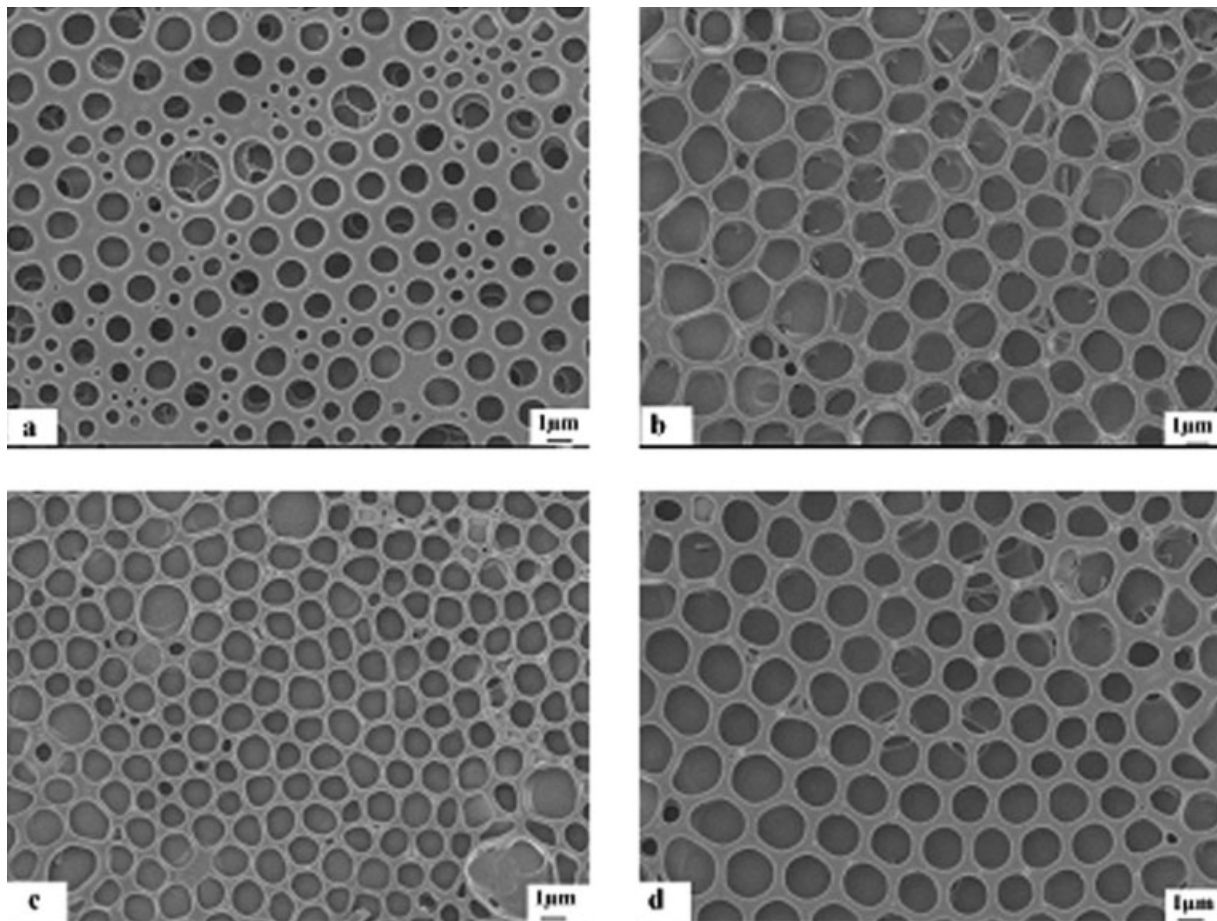


Figure 6 SEM images of porous structure in PEEK-NO₂ films prepared from different percent mixed solvents. Volume ratio of the solvents: CHCl₃ : CH₂Cl₂ = (a) 100 : 0; (b) 0 : 100; (c) 70 : 30; (d) 50 : 50. Other conditions: temperature: 30°C; relative humidity: 95%; concentration: 2 g/L; spreading volume: 100 μL.

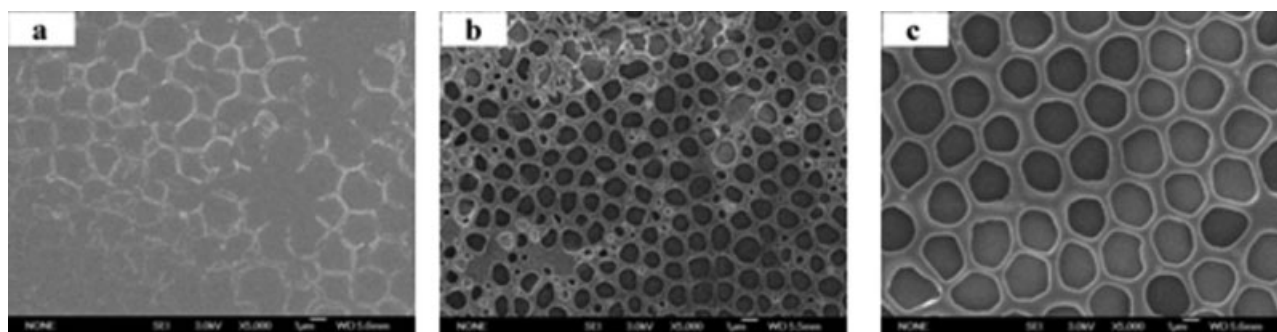


Figure 7 SEM images of porous structure in PEEK-NO₂ films prepared under different relative humidity conditions. (a) 45%; (b) 80%; (c) 95%. Other conditions: temperature: 30°C; concentration: 1 g/L; spreading volume: 100 μL.

Figure 6 shows the SEM images of PEEK-NO₂ prepared in mixed solvents (CH₂Cl₂ and CHCl₃). It can be seen that PEEK-NO₂/CHCl₃ or PEEK-NO₂/CH₂Cl₂ solution formed porous structure, but the pores were irregular (6a, 6b). It is because PEEK-NO₂ could not stabilize at the interface of solvent–water, then the water droplets could accumulate and assemble to form pore easily. Thereby, the size of the pores became diversiform and ideal pore structures could not be obtained.

Adjusting the volume ratio of the mixed solvents, when CHCl₃ : CH₂Cl₂ = 50 : 50, the obtained pore structure was regular and the size was homogeneous. The reason is that regular pore structure can be obtained easily in solvents that had good intersolubility and appropriate volatility. Although CH₂Cl₂ and CHCl₃ were both favorable solvents of PEEK-NO₂, CH₂Cl₂ (bp = 40°C) evaporated faster than CHCl₃ (bp = 61.5°C). Through adjusting the mixed solvents to an appropriate volume ratio, the volatility of the mixed solvents increased and the time that the film liquid need to solidify shortened. So, the collision among the water droplets could stop as the solidifying of the film liquid and more regular pore structure could be obtained.

Influence of atmosphere humidity to the formation of regular pore structure

Figure 7 shows the SEM images of films that are obtained under different relative humidity conditions. It can be seen that with the decrease of the atmosphere humidity, the aperture diminished, the regularity of the pore structure lowered, and even no pore appeared. The reason is that under low humidity, there were not enough water droplets to pledge the growth of the condensed water droplets on the film surface, so the obtained pore diameter were small and the structures were less regular. The atmosphere humidity was a key factor that could influence the formation of the honeycomb structure,

and it was also one of the factors that could control the size of the aperture.

CONCLUSIONS

Honeycomb film was prepared based on PEEK-NO₂, which was prepared through acid (nitric acid and sulfuric acid) nitration from PEEK. The influence factors on the pattern formation and fabrication of the porous structure, such as the solution concentration, the solvent, and the atmosphere humidity, were investigated. It is found that with the increase of the solution concentration, the aperture of the film diminished gradually. The lower the solvents' boiling point were, the smaller the film apertures were and the more regular the pores arrange. Only under high-humidity circumstances could obvious and ordered honeycomb films be formed.

References

1. Shimomura, M.; Sawadaishi, T. *Colloid Interface Sci* 2001, 6, 11.
2. Widawski, G.; Rawiso, B.; Frangois, B. *Nature* 1994, 369, 387.
3. Frangois, B.; Pitois, O.; Frangois, J. *Adv Mater* 1995, 7, 1041.
4. Pitois, O.; Frangois, B. *Eur Phys* 1999, 138, 225.
5. Shimomura, M. *Prog Polym Sci* 1993, 18, 295.
6. Deleuze, H.; Schultze, X.; Sherrington, D. C. *Polymer* 1998, 39, 6109.
7. Nishikawa, T.; Nonomura, M.; Arai, K.; Hayashi, J.; Sawadaishi, T.; Nishiura, Y. *Langmuir* 2003, 19, 6193.
8. Nishikawa, T.; Arai, K.; Hara, M.; Shimomura, M. *Mater Res Soc Symp Proc* 2002, 72, 229.
9. Chen, C. X.; Tian, Y.; Shi, Y. Q.; Tang, R. P.; Xi, F. *Langmuir* 2005, 21, 6576.
10. Chen, C. X.; Tian, Y.; Shi, Y. Q.; Tang, R. P.; Xi, F. *Macromol Rapid Commun* 2005, 26, 1266.
11. Gover, L. V.; Bashmakov, I. A.; Kaputski, F. N.; Pientka, M.; Parisi, J. *Macromol Chem Phys* 2000, 201, 1721.
12. Gover, L. V.; Bashmakov, I. A.; Kiebooms, R.; Dyakonov, V.; Parisi, J. *Adv Mater* 2001, 13, 588.
13. Yu, C. L.; Zhai, J.; Gao, X. F.; Wan, M. X.; Jiang, L.; Li, T. J. *Phys Chem B* 2004, 108, 4586.
14. Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv Mater* 2000, 12, 1841.

15. Lijima, K.; Tomita, Y. *Appl Phys* 1986, 60, 361.
16. Liu, Y. S. *Metall Anal* 1992, 12, 37.
17. Kojima, M.; Okuyama, M. K.; Nakagawa, T. *Jpn J Appl Phys* 1983, 22, 14.
18. Sun, W.; Li, Y. X.; Ren, W. *Ferroelectrics* 1990, 108, 9.
19. Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interaction and the Miscibility of Polymer Blends*; Technomic Publishing Co.: Lancaster, 1991.
20. Smith, P.; Hara, M.; Eisenberg, A. *Curr Top Polym Sci* 1987, 2, 6.
21. Chen, C. T.; Morawetz, H. *Macromolecules* 1989, 22, 159.
22. Jeong, H. J.; Oishi, Y.; Kakimoto, M. A.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1990, 28, 3293.
23. Wang, F.; Chen, T.; Xu, J. *Macromol Chem Phys* 1998, 199, 1421.
24. Tian, Y.; Jiao, Q. Z.; Ding, H. Y.; Shi, Y. Q.; Liu, B. Q. *Polymer* 2006, 47, 3866.
25. Tian, Y.; Ding, H. Y.; Jiao, Q. Z.; Shi, Y. Q. *Macromol Chem Phys* 2006, 207, 545.