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Green Synthesis of Polyimides and Their CNT Based Nanohybrid Shish-Kebabs through Reaction-induced Crystallization of Nylon-salt-type Monomers in Glycerol*

Xiao-juan Li[a], Lu Chen[a], Wei Huang[a], Xiang Li[a], Chao-liang Zhang[b] and Xi-kui Liu[a**]
[a] *College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China*
[b] *State Key Laboratory of Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu 610065, China*

Abstract A green approach to the synthesis and morphological control of high performance polyimides and their nanohybrid shish-kebabs in glycerol through reaction-induced crystallization of nylon-salt-type monomers was reported. Crystalline polyimide nanoplates can be observed by direct polycondensation of pyromellitic acid with various kinds of aliphatic or aromatic diamines. With the existence of carbon nanotubes, the polyimides can be successfully decorated on the surface of CNTs through a reaction-induced hetero-epitaxial crystallization process, and resulted in novel polyimide/CNT nanohybrid shish-kebabs (NHSKs) structures. The morphologies of the NHSKs can be fine-tuned through changing the concentration of monomers or the reaction temperature, especially through the introduction of dynamic imine chemistry, the formation process of NHSKs can be attributed to a soft epitaxy mechanism. Thus a green approach for the synthesis of high performance polyimides and their CNT based nanohybrid structures was explored, which should be of great value for their applications in high performance reinforced nanocomposites.

Keywords: Polyimides; Reaction-induced crystallization; Nanohybrid shish-kebabs; Green synthesis.

INTRODUCTION

Polyimide (PI) is one of the high performance polymers which exhibited excellent thermal properties, mechanical properties and electrical properties, and thus has broad applications in the fields like aerospace, automotive, microelectronics and so on[1, 2]. The successful application of polyimides requires not only synthesis new materials with various chemical structures, but also needs to precisely control over their crystal morphology and architectures. However, due to their insolubility and infusibility, the morphology control of polyimides is very difficult. Recently, Kimura developed reaction induced crystallization as a powerful strategy for the morphology control of aromatic polymers to overcome the antagonistic problem between intractability and morphology control, polyimides and polyazomethines with nanosheet, nanofiber and nanoflower-like crystalline structures which are very difficult to obtain through conventional methods have been successfully prepared[3–5]. Our group have also carried out series of studies on the aromatic polymer controllable morphologies based on the reaction-induced crystallization, with the introduction of novel dynamic covalent chemistry[6–8], we can achieve precise control the crystallization behavior and crystalline architectures of aromatic polymers[9–11].

It is known that carbon nanotubes (CNTs) show good nucleation ability for crystallization of many kinds of polymers[12–14], adding CNTs as foreign nucleating agent can further strengthen the nucleation and growth of the

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** Corresponding author: Xi-kui Liu (刘习奎), E-mail: xkliu@scu.edu.cn
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aromatic polymer crystals, besides, the crystallization of polymers on the surface of CNTs results in hybrid crystal structures, thereby greatly promotes their application as advanced composite materials and functional materials. For example, Li obtained a novel kind of nanohybrid shish-kebab (NHSK) structures through solution crystallization of polyethylene and nylon-66 on the surface of CNTs, and conducted in-depth study of its epitaxial crystallization mechanism[15–18]. Fu *et al*.[19, 20] and Li *et al*.[21, 22] have also made outstanding contributions to the controlled formation of NHSKs using industrialized processing methods. Most of the polymers studied so far are commercial polymers like polyolefin or aliphatic polyesters. In order to make more efficient use of the excellent mechanical properties and optoelectronic properties of the polymer, very recently, Li group[23] and our group[11] found that reaction-induced epitaxial crystallization can effectively achieve the epitaxial crystallization of insoluble high-performance polymers like PTFE and polyimide on the surface of CNTs, the obtained high performance polymer based NHSK structures are valuable for the applications in high temperature environments.

Taking account of the increasing atmospheric pollution and growing concerns on environmental issues, green chemistry has drawn highly academic and industrial interests in recent decades[24]. Among them, volatile organic compounds are the main reason for water and air pollution, thus the search for the substitution of volatile organic solvents has become an emergency task. Polyimides are generally obtained using high-boiling aprotic solvents such as *N*-methyl pyrrolidone, dimethylformamide, cresol and dibenzyltoluene, all of these solvents are hazardous to environment, thus green synthesis routes towards polyimides would be of great interest. Recently, Antonietti and Weber[25] studied the synthesis of aromatic PIs under hydrothermal conditions, besides Watanabe[26] reported the preparation of aliphatic polyimide particles in ethylene glycol through polycondensations of nylon-salt-type monomers composed of diethyl pyromellitate and aliphatic diamines.

In this communication, we propose a green synthesis approach for polyimides and their carbon nanotube based hybrid nanohybrid shish-kebabs in glycerol through reaction-induced crystallization of nylon-salt-type monomers. Crystalline polyimide nanoplates can be observed by direct polycondensation of pyromellitic acid with various kinds of aliphatic or aromatic diamines. With the existence of carbon nanotubes, the polyimides can be successfully decorated on the surface of CNTs through a reaction-induced hetero-epitaxial crystallization process, and resulted in novel polyimide/CNT nanohybrid shish-kebabs structures. Besides, we also observed the dynamic imine chemistry can help controlling the epitaxial process and thus controlling the morphologies of resulted NHSKs. The research opened a new gateway for the surface modification of CNTs using high performance aromatic polymers, which is of great value for the application in high performance reinforced nanocomposites.

EXPERIMENTAL

Materials

Hexamethylene diamine (HMDA), benzaldehyde, *p*-phenylenediamine (PDA), benzidine (BZD) and glycerol were purchased from Chengdu Kelong Co. Ltd. PDA and BZD were purified by sublime before use. Pyromellitic acid (PMA) was obtained by the hydrolysis of pyromellitic dianhydride (purchased from Shanghai Institute of Synthetic Resins) according to the standard procedure. Multi-walled carbon nanotubes (CNTs) with diameter of 30−50 nm and length of 10−20 um were obtained from Timesnano Co. Ltd, which is produced by natural gas catalytic decomposition over Ni-based catalyst, followed by further oxidation in $KMnO_4$/HCl solution to afford a carboxyl content of 0.73%.

Synthesis of Polyimides by Reaction Induced Crystallization in Glycerol Solvent

A cylindrical flask containing 10 mL glycerol solvent was heated under a slow stream of nitrogen up to the designated temperature, PMA was added and dissolved completely in several seconds with stirring, equal mole of diamine was then added into the solution, reaction-induced crystallization process was carried out at this temperature for 6 h. After that, the resulted products were separated by centrifugation and washed several times with distilled water and ethanol, then dried in vacuum at 80 °C for 12 h.

Preparation of PI/CNT NHSKs through Reaction Induced Hetero-epitaxial Crystallization on Carbon Nanotubes

2.0 mg CNTs were added into mortar with 10 mL glycerol solvent, then grinded for 0.5 h to exfoliate the CNT bundles and formed a uniform black suspension, the solution was poured into a cylindrical flask and then heated under a slow stream of nitrogen up to the designated temperature with gentle stirring, PMA was added and dissolved completely in several seconds, equal mole of diamine was then added into the solution, the process was carried out at this temperature for 6 h under gentle stirring. After reaction, the resulted NHSKs were separated by centrifugation and washed several times with distilled water and ethanol, then dried in vacuum at 80 °C for 12 h.

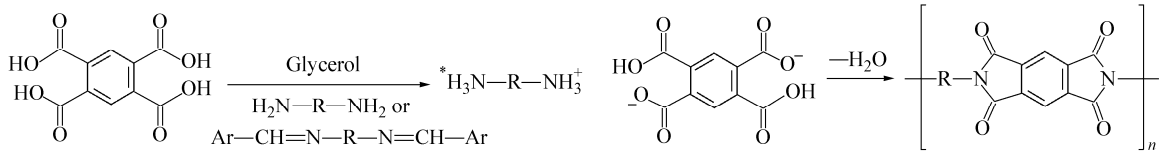
The dynamic chemistry controlled reaction-induced epitaxial crystallization process is as mentioned above with some variation: the diamine was first react with benzaldehyde at 150 °C for 2 h to form a constitutional dynamic imine mixtures in glycerol/CNT solution, then the solution was heated to the reaction temperature, PMA was then added to finish the epitaxial crystallization process.

Measurements

The chemical structures were characterized by infrared (IR) spectra with a Nicolet 560 spectrometer, the morphology of the PIs and their NHSKs were observed by SEM (Inspect F scanning electron microscope at 20 kV). WAXS powder patterns were recorded on an x-pert pro MPD diffractometer at 30 kV and 15 mA with a scanning rate of 1 (°) min^{-1}. The degree of crystallinity was calculated based on the areas of crystalline peaks and amorphous halo by the software of x-pert pro MPD diffractometer.

RESULTS AND DISCUSSION

Polyimides were prepared by nylon-salt-type monomers derived from pyromellitic acid and various diamines, the nylon-salt-type monomer is an extremely reactive and facile approach for the preparation of polyimides in a very short reaction time. Glycerol was chosen as the solvent for the preparation of polyimides, this is because glycerol is a colorless, odorless and viscous liquid with high boiling point (290 °C), besides, glycerol costs cheaper[27]. The chemical process for the preparation of polyimides is shown in Scheme 1, where the pyromellitic acid quickly reacts with diamine and forms the nylon-salt precursor, which is then quickly cyclization to form polyimide under high temperature with the elimination of water.



Scheme 1 Preparation of PIs through nylon-salt monomers in glycerol solvent

The processes were carried out at 220 °C in glycerol at a concentration of 0.4%. Soon after the addition of PMA and diamine, the solutions became turbid due to the reaction induced crystallization and precipitation of PIs, the process was kept at this temperature for 6 h to finish the imidization process. The resulted products were collected by centrifugation and washed several times with distilled water and ethanol then dried in vacuum at 80 °C for 12 h, with a yield about 90%, the morphologies of the formed PIs were characterized by SEM. (Fig. 1).

As shown in Fig. 1, the PIs obtained from glycerol are generally composed of lamellae structure, PMA-HMDA polyimide are very big microplates with diameter about ten micrometers (Fig. 1a). PMA-PDA polyimide is curved microplates (Fig. 1b), while for PMA-BZD polyimide, uniform flower-like morphology composed of crystalline nanoplates was formed (Fig. 1c).

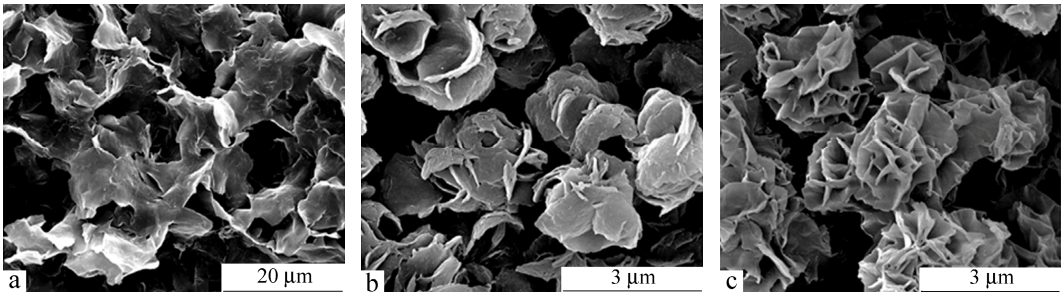


Fig. 1 SEM images of PIs prepared by reaction-induced crystallization from PMA and various diamines: (a) 1,6-diaminohexane, (b) PDA and (c) BZD at 220 °C and concentration 0.4% in glycerol for 6 h

The structures of the resulted polyimides were also characterized to confirm the formation of fully imidized polymers. Due to the poor solubility of polyimide in most of organic solvents, their chemical structure was mainly analyzed by FTIR spectroscopy (Fig. 2a). All the polyimides prepared showed characterized bands at about 1770 and 1370 cm^{-1} corresponding to imide bonding; meanwhile the bands attributed to the monomers (carboxyl and amino groups) were absent or strongly attenuated in the spectrum, thus the successful preparation of polyimides was confirmed. Powder X-ray diffraction patterns reveal the crystalline nature of the PIs prepared in glycerol (Fig. 2b), the PI from PMA and HMDA shows a semi-crystalline nature with peaks at 2θ of about 6° and 20°, the latter corresponds to the inter-chains distance which is common in polymers, while the former at lower angle corresponds to the repeating unit of the semi-aromatic polyimide. The full aromatic polyimides from PMA and PDA or BZD show a much higher degree of crystallinity, sharp reflections corresponding to crystals can be clearly observed.

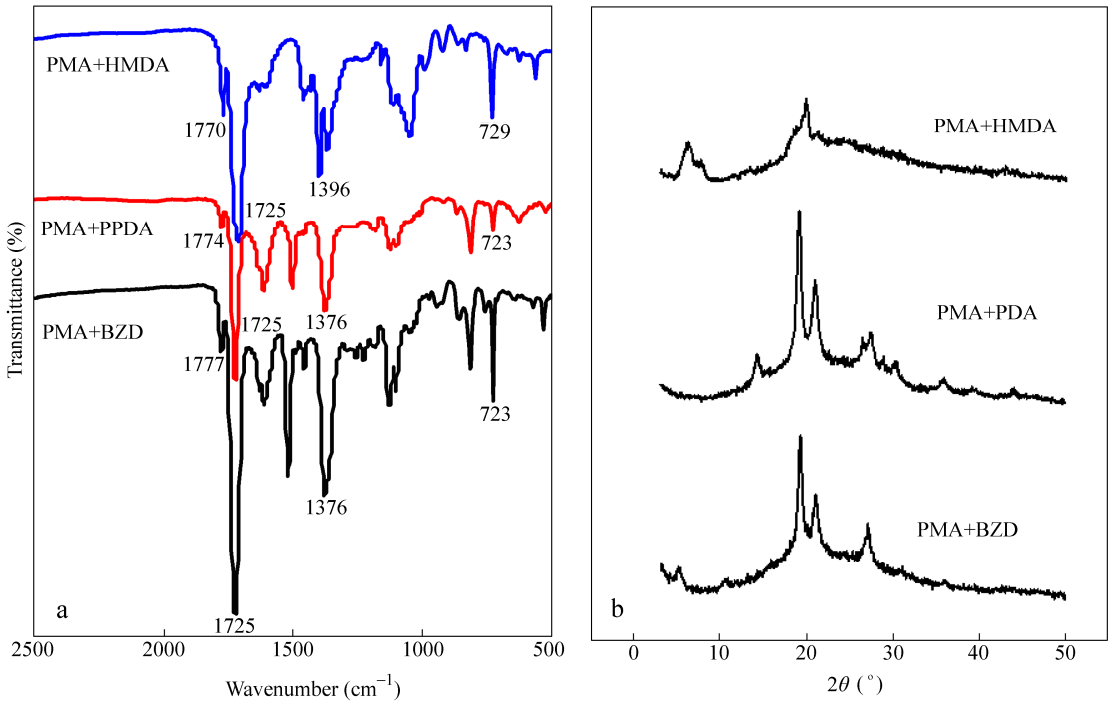


Fig. 2 FTIR spectra (a) and WAXS patterns (b) of PIs prepared from PMA-HDMA, PMA-PDA and PMA-BZD at a concentration of 0.4% and 220 °C for 6 h

The crystallization behavior of polymers using CNTs as nucleating agent has become an attractive topic in polymer field. We have previously reported the reaction-induced epitaxial crystallization of polyimide on the surface of CNTs in a high boiling point organic solvent; here we attempt to extend this method in the green glycerol solvent. Direct polymerization of PMA and diamine in glycerol resulted in microplates or microflowers, however, when CNTs were added into the solution, the morphologies were totally changed.

As can be clearly observed in Fig. 3, in the presence of CNTs, PI from PMA-PDA resulted in a mixture of CNTs and PI nanoplates, no nucleating of PI on the surface of CNTs can be observed (Fig. 3b). However, for PI from PMA-HMDA and PMA-BZD, SEM revealed most of the CNTs were periodically decorated by polyimide crystals (Figs. 3a, 3c). Fully aromatic polyimides have excellent thermal and mechanical properties, thus we focused on how to control the formation of more ordered and pure PI/CNT NHSKs using fully aromatic PMDA-BZD polyimide. The influence of reaction factors was investigated in detail. Previous studies have revealed that the reaction temperature has a dominant effect on the crystallization behavior of polymer during reaction induce crystallization process, so we studied the influence of reaction temperature on the epitaxial growth of PI on the surface of CNTs.

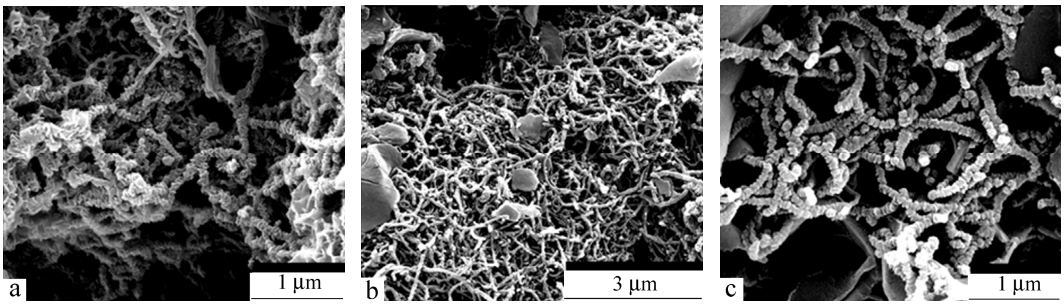


Fig. 3 SEM images of PI NHSKs prepared by reaction-induced epitaxial crystallization with CNTs as foreign nucleate agent at 220 °C and concentration 0.4% in glycerol for 6 h: (a) PMA-HMDA, (b) PMA-PDA and (c) PMA-BZD

As shown in Fig. 4, when reaction takes place at 190 °C, a mixture of PI nanoplates, bare CNTs and NHSKs can be observed, which means many of the PIs crystallized by themselves instead of epitaxial growth on the surface of CNTs (Fig. 4a). When temperature increases to 220 °C, a mixture of pure polyimide crystalline microplate and NHSKs still can be observed, however, the NHSKs are more uniform than those prepared at 190 °C. When the reaction temperature further rises up to 250 °C, more uniform NHSKs were obtained, with a small amount of pure polyimide nanoplates, however pure NHSKs are still not available.

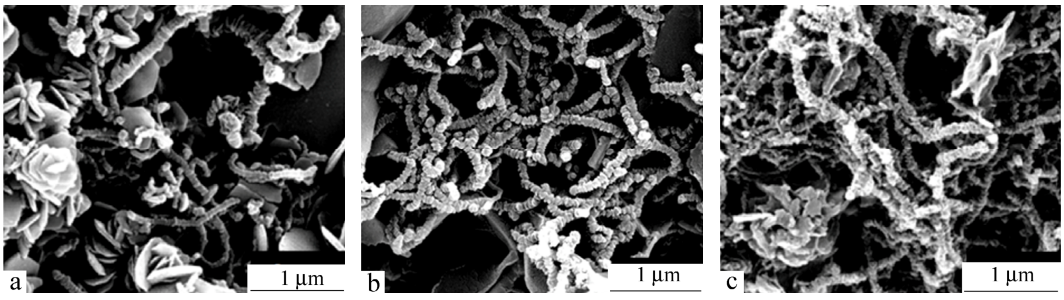


Fig. 4 SEM images of PI/CNT NHSKs prepared from PMA and BZD with CNTs as foreign nucleate agent at a conc. of 0.4% and temperature of (a) 190 °C, (b) 220 °C and (c) 250 °C

Previous studies in our group have demonstrated that the introduction of constitutional dynamic imine chemistry is a powerful method to control the kinetics of reaction induced crystallization process[9–11], thus,

instead of direct reaction with PMA, the BZD was first reacted with benzaldehyde to form a dynamic constitutional imine mixture, and then the PMA was added to begin the epitaxial process. SEM revealed pure NHSKs with the CNTs decorated with uniform crystalline PI discs as the only products were formed (Fig. 5), the PI discs have a bigger diameter than the control ones, and with a bigger periodical distance, thus revealing the constitutional imine chemistry can be a powerful strategy for the morphology fine-tuning of NHSK structures.

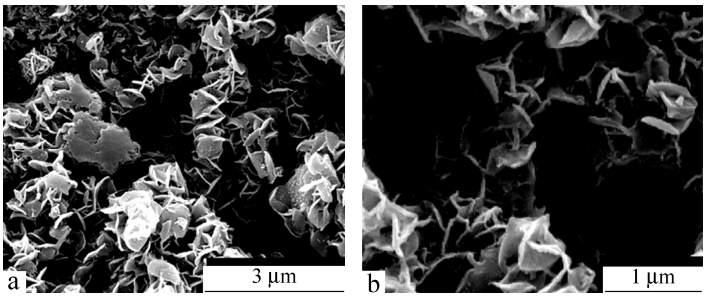


Fig. 5 SEM image (a) and enlarged image (b) of PI/CNT NHSKs prepared from PMA and BZD with the assistance of constitutional dynamic imine chemistry at temperature of 220 °C and conc. of 0.4% for 6 h

The influence of the monomer concentrations on the growth of NHSK structures was also investigated, when the concentration was 0.2%, immature hybrid structure with some nanoparticles growth on the surface of CNTs was observed. Increase the monomer concentration to 0.4%, uniform NHSKs with PI crystals discs were formed. However, when the concentration was increased to 0.8%, due to the overgrowth of polyimide crystals, we can't find typical CNTs based nanohybrid shish-kebab morphology, instead, secondary nucleation on the intial formed nanoplate resulting in complex structures was observed (Fig. 6). Due to their outstanding thermal stability and high char yields, the above prepared aromatic polyimides/CNT hybrid structures may provide a powerful approach for the preparation of nanostructured carbons.

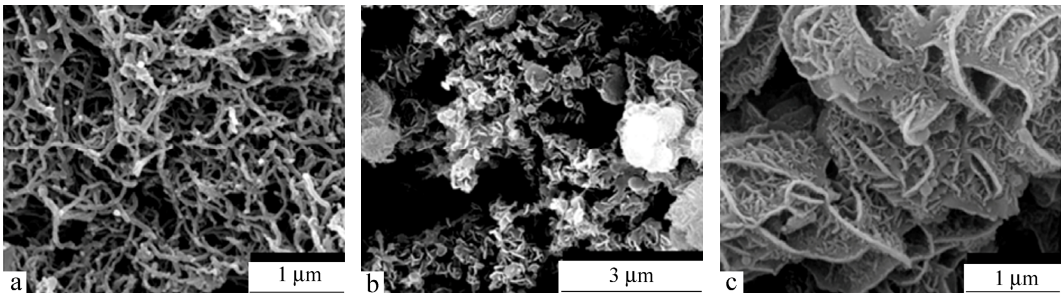


Fig. 6 SEM images of PI/CNT NHSKs prepared from PMA and BZD with the assistance of constitutional dynamic imine chemistry at temperature of 220 °C for 6 h and at conc. of (a) 0.2%, (b) 0.4% and (c) 0.8%

We further studied the formation process of NHSKs at different stages to explore the growing process and formation mechanism behind this novel reaction induced epitaxial crystallization. At the early stage of the reaction of about 15 min, we can observe lots of bare CNTs, however, a few polyimide discs can be found grown on the CNTs to form a shish-kebab like structure (Fig. 7a). With the reaction proceeds to about 30 min, uniform NHSK superstructure can be clearly observed, no bare CNTs can be detected (Fig. 7b). These uniform NHSK superstructures were kept during the following thermal process (Fig. 7c).

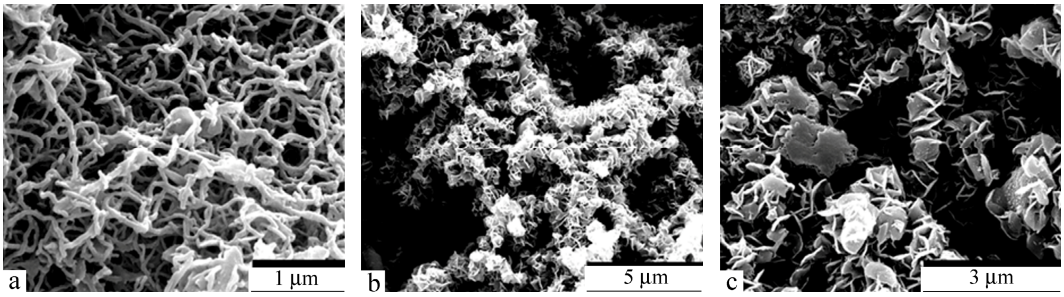
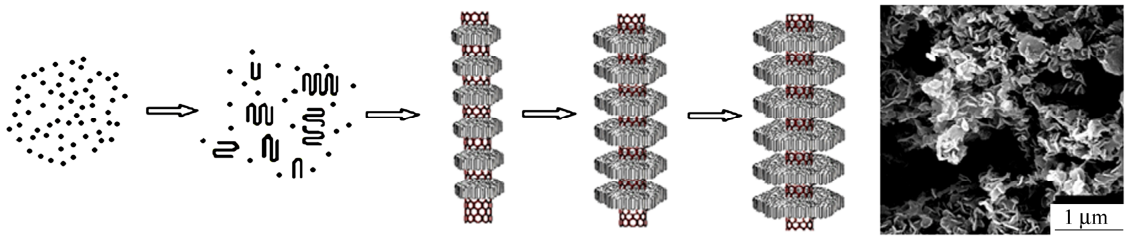


Fig. 7 SEM images of PI/CNT NHSKs prepared from PMA and BZD with the assistance of constitutional dynamic imine chemistry at 220 °C with conc. of 0.4% for 6 h at different time stages: (a) 15 min, (b) 30 min and (c) 60 min

Even it has been known for a long time that the surface of fillers plays a key role in the formation of hybrid crystalline structures, however a universal formation mechanism for each kind of hybrid crystalline structure is still not available. Li proposed a formation mechanism of NHSKs based on the soft epitaxial crystallization of polymers on the surface of nanometer sized CNTs, where a strict lattice matching is not needed. Due to the loosely packing of PI discs on the surface of CNTs, we can clearly identified that almost all the crystal polymer discs are perpendicular to the CNT shish axis, disregarding the experimental parameters, thus we believed this soft epitaxy growth mechanism proposed by Li *et al*. is also the case for the formation of nanohybrid shish-kebabs in this reaction-induced epitaxial crystallization process, a main difference maybe the initial nuclei were formed by the crystallization of aromatic oligomers *in situ* formed by polycondensation. Thus the formation process can be described as follows (Scheme 2): right after the monomers were added into glycerol at high temperatures, they begin to react and form oligoimides, when the degree of polymerization reached a critical value, they will precipitate and crystallize from the solution and nucleate on the surface of CNTs, further growth of oligomers perpendicular to the CNTs resulted in the formation of NHSK structures, besides, under the prolonging thermal treatment, the oligoimides will gradually form polyimide with high molecular weight through solid state polycondensation.



Scheme 2 Schematic representation of the formation of nanohybrid shish-kebabs through reaction-induced epitaxial process in glycerol solvent

Since their discovery, NHSKs have attracted tremendous attention due to their unique hybrid structures; besides, it provides a unique approach for the CNTs patterning and modification. However, so far, most of the polymers used to prepare NHSKs are thermoplastics such as polyethylene, polypropylene or nylon, their low thermal stability may limit their potential applications. The thermal stability of these polyimides and their corresponding NHSKs obtained in glycerol was measured by TGA in nitrogen atmosphere, the thermogravimetric analyses revealed the initial decomposition temperature of PMA-BZD polyimide and their NHSKs was about 570 °C and 552 °C respectively, thus the resulted PI based nanohybrid shish-kebabs have good thermal stability which offers a great advantage in application fields like high temperature resistant reinforced composites.

CONCLUSIONS

In summary, we reported a green approach for the synthesis and morphological control of high performance polyimides in glycerol through reaction-induced crystallization of nylon-salt-type monomers. Crystalline polyimide nanoplates with flower-like morphology can be obtained through direct polymerization of monomers. With the existence of carbon nanotubes, the polyimides can successfully decorate on the surface of CNTs through a reaction-induced hetero-epitaxial crystallization process, and resulted in novel PI/CNT nanohybrid shish-kebab structures wherein the CNT serves as the shish and polyimides crystals as the kebabs. The diameters and the periodical distances can be effectively controlled through fine-tuning the reaction parameters, especially with the introduction of constitutional dynamic imine chemistry. The formation process of polyimide/CNT NHSKs can be attributed to a "soft-epitaxy" mechanism, providing a green approach for the preparation of polyimide and their CNT based hybrid structures. We believe this simple, novel and green reaction induced epitaxial crystallization will open a gateway for creating aromatic polymer based hybrid hierarchical micro-nanoarchitectures, which have great advantages in applications such as high temperature resistant reinforced nanocomposites and opto-electronics.

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