



Helical polyurethane@attapulgit nanocomposite: Preparation, characterization and study of optical activity

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ARTICLE INFO

Article history:

Received 6 January 2009

Received in revised form

5 April 2009

Accepted 28 May 2009

Available online 3 June 2009

Keywords:

Polyurethane

Attapulgit

Helical structure

Optical activity

Nanocomposite

ABSTRACT

Helical polyurethane@attapulgit (BM-ATT) based on R-1,1'-binaphthyl-2',2'-diol (R-BINOL) composite was prepared after the surface modification of attapulgit (ATT). BM-ATT was characterized by Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HTEM) and vibrational circular dichroism (VCD) spectroscopy. FT-IR and XRD analyses indicate that the helical polyurethane has been successfully grafted onto the surfaces of the modified ATT without destroying the original crystalline structure of ATT. BM-ATT exhibits the rod-like structure by SEM, TEM, and HTEM photographs. BM-ATT displays obvious Cotton effect for some absorbance in VCD spectrum, and its optical activity results from the singlehanded conformation of helical polyurethane.

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1. Introduction

Recently the focus has turned on the natural clay minerals, including montmorillonite [1], kaolin [2], mica [3], smectite [4] attapulgit [5] and sericite [6], for the preparation of nanocomposites due to their low-cost and unique properties. Attapulgit (ATT) is a kind of crystalline hydrated magnesium aluminum silicate with unique three dimensional structures and has a fibrous morphology with exchangeable cations and reactive -OH groups on its surface. ATT has the structural formula $\text{Si}_8\text{O}_{20}\text{Mg}_5(\text{Al})(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ and its ideal structure is studied by Bradley early in 1940. Because of its structural morphology and high surface areas, ATT has received considerable attention with regard to the adsorption and the removal of heavy metal ions [7–9], but there are few reports about its use in the nanocomposites grafted with helical polymers.

Helical polymers are special polymers, which possess not only the advantages of polymers such as low density, high strength, tractability, and so on, but the unique optical activity. Their unique helical structure and optical activity provide the possibility to use helical polymers in many applications. Helical polymers and their composites have attracted great attention due to their helical structure, various supramolecular architectures, and, more importantly, their potential applications in chiral and sensing materials, molecular switches, data storage, optical devices, chromatographic chiral separation, and liquid crystals display

[10–17]. The synthetic polymers with right or left-handed conformation can be optically active without any chiral component. This is because these polymers contain singlehanded helical chains and they are chiral essentially [18]. If the polymer backbone is rigid enough, or the steric repulsion of side groups is large enough to maintain a stable conformation, there is the possibility of obtaining helical optical polymers. Binaphthyl units can just provide the rigid backbone and the chiral origin due to its axial chirality and conformational stability [19–21]. In this paper, helical polyurethane@attapulgit (BM-ATT) nanocomposite based on R-1,1'-binaphthyl-2',2'-diol (R-BINOL) was prepared and characterized. BM-ATT exhibits rod-like structure and it is coated by an optically active shell. BM-ATT possesses many potential applications in chiral and sensing materials, optical devices and so on owing to its optical activity.

2. Experimental section

2.1. Materials

Attapulgit, provided by Hong-fei Company (Jiangsu, China), was treated with 36.5% hydrochloric acid for 24 h, followed by washing with distilled water until pH 6.5 and drying in vacuum at 50 °C for 24 h. R-1,1'-binaphthyl-2',2'-diol was synthesized and separated according to the literature [22,23]. 4,4'-diphenylmethane diisocyanate (MDI, TCI Co. Ltd.) was dried and purified under vacuum. N,N-dimethylformamide (DMF, Shanghai Chemical Reagent Co.) was dried over 40 nm molecular sieves

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for 1 week. Other solvents were all obtained from Shanghai Chemical Reagent Company and used as received without further purification.

2.2. Preparation of MDI-ATT (M-ATT)

Two grams of ATT and 10 mL DMF solution of 0.5 g MDI dispersed into 80 mL dried toluene with ultrasonic agitation for 1 h in a 250 mL flask and the ultrasound power was 600 W. After that the mixture was refluxed at 100 °C for 8 h with stirrer, condenser, and nitrogen inlet. After cooling to room temperature, the mixture was filtered and thereafter thoroughly washed with acetone. Then it was dried in vacuum at 40 °C for 12 h to obtain the M-ATT. The process is shown in Fig. 1(1).

2.3. Preparation of helical polyurethane@attapulgate based on R-BINOL

Forty millilitres of DMF solution of 1.144 g R-BINOL was firstly conducted in a 150 mL four-necked round-bottom flask equipped with stirrer, condenser, nitrogen inlet, and heated to 100 °C gradually. Then, 10 mL DMF solution of 0.5 g MDI was added into the reactor drop by drop slowly at 100 °C and reacted for 5 h to obtain the prepolymer. Then, M-ATT was dispersed into reactor and reacted at 100 °C for 6 h. After cooling to room temperature, the mixture was centrifugalized at the speed of 3000 r/min. After taking off the upper layer floccules, the product was thoroughly washed with ethanol and dried in vacuum at 40 °C for 24 h to obtain BM-ATT. Fig. 1(2) displays the scheme of this process.

2.4. Measurements

FT-IR spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer at room temperature using KBr pellets. FT-IR spectra were obtained at a 4 cm⁻¹ resolution and recorded in the region of 4000–400 cm⁻¹. The samples and background scanning times

were both 16. Thermal analysis experiments were performed using a TGA apparatus operated in the conventional TGA mode (TA Q-600, TA Instrument) at the heating rate of 10 K/min in a nitrogen atmosphere and sample size was about 50 mg. X-ray diffraction (XRD) measurements were recorded using a Rigaku D/MAX-R with a copper target at 40 kV and 30 mA. The power samples were spread on a sample holder and the diffractograms were recorded in the range 5–70° at the speed of 5°/min. Transmission electron microscopy (TEM) was performed with a Hitachi H-600 microscope operating at 120 kV. High resolution transmission electron microscopy (HTEM) was performed with a JEM-2010 UHR microscope operating at 200 kV. Samples were prepared by placing drops of the colloids dispersion on a Cu grid (200 mesh; placed onto filter paper to remove excess solvent) and allowing the solvent to evaporate at room temperature. Scanning electron microscopy (SEM) was obtained on the microscope of LEO-1530VP. Vibrational circular dichroism (VCD) spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer attached by PMA50 (Bruker) at room temperature using KBr pellets and the scanning time is 8 h.

3. Results and discussion

3.1. FT-IR analysis

Fig. 2 shows the FT-IR spectra of (a) ATT, (b) M-ATT and (c) BM-ATT. After the assembly of MDI to ATT, the 2270 cm⁻¹ band of isocyanate groups is found in the FT-IR spectrum of the MDI-ATT (Fig. 2b). This result indicates that when a diisocyanate molecule is linked to surface of ATT by the reaction between one isocyanate and –OH on the surface of ATT, the remaining isocyanate group is unlikely to react with other ATT due to the reduced reactivity of immobilized molecules [24]. In addition, the absorptions of amide I and amide II appear at 1545 and 1512 cm⁻¹, respectively, and the absorption band of C=O is overlapped by asymmetric –COO stretching and results in a broad absorption band at about

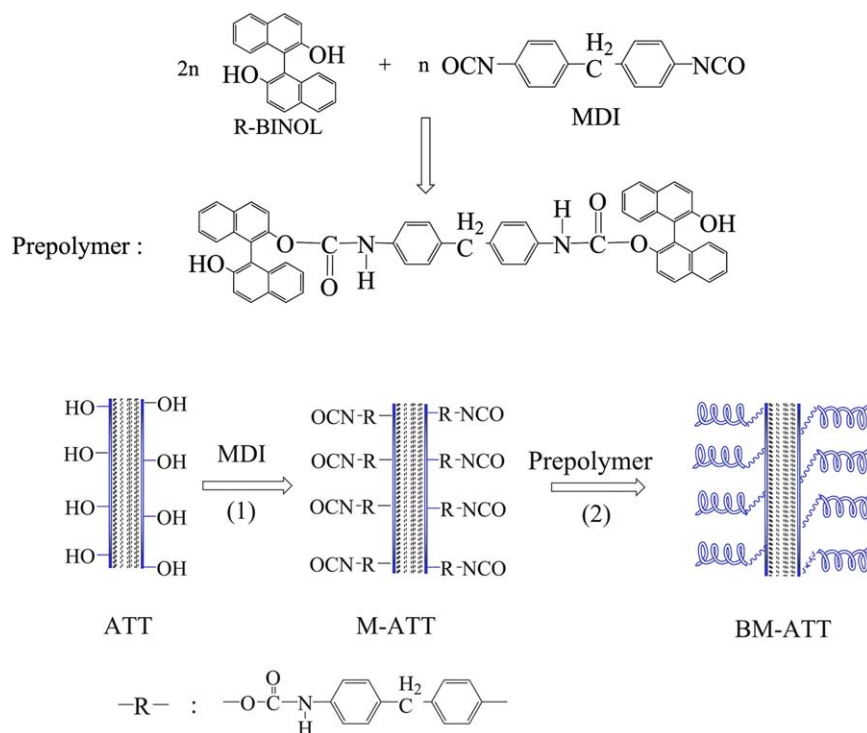


Fig. 1. The scheme of preparation of BM-ATT.

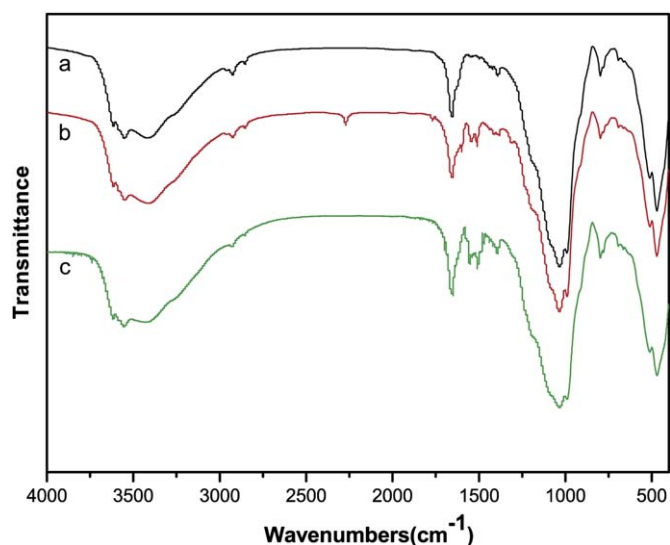


Fig. 2. FT-IR spectra of (a) ATT, (b) M-ATT, and (c) BM-ATT.

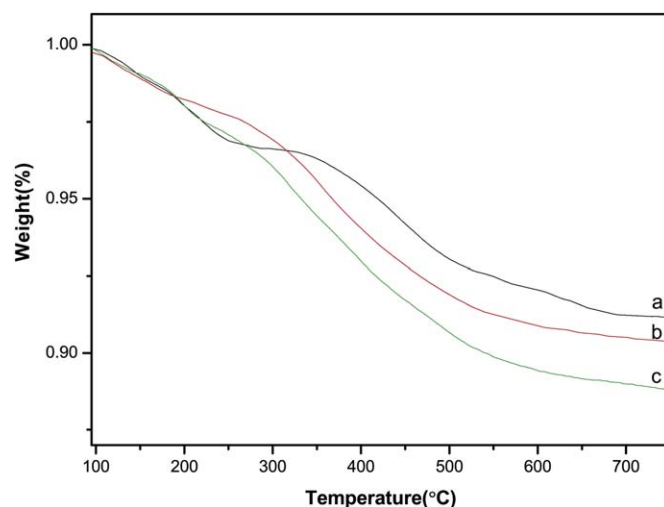


Fig. 4. TG curves of (a) ATT, (b) M-ATT, and (c) BM-ATT.

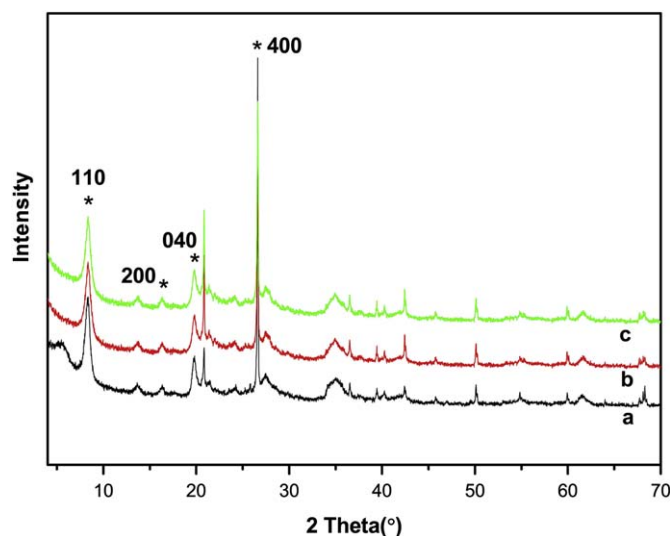


Fig. 3. XRD patterns of (a) ATT, (b) M-ATT, and (c) BM-ATT.

1610 cm^{-1} [25]. As can be seen in Fig. 2c, after grafting with prepolymer by the hydrogen transfer addition reaction, the band at 2270 cm^{-1} disappears, and the absorptions of amides are enhanced. It can be concluded from Fig. 2 that the graft reaction has taken place as expected.

3.2. Crystalline structure analysis

The samples are also analysed by X-ray powder diffraction (XRD) and the patterns of ATT, M-ATT and BM-ATT composites are presented in Fig. 3. The diffraction peaks at $2\theta = 8.3, 13.6, 19.7,$ and 26.6° correspond to the primary diffraction of the (110), (200), (040), and (400) planes of the clay, respectively. The similarity of the XRD patterns between ATT (a), M-ATT (b) and BM-ATT (c) indicates that the original crystalline structure of ATT has not been destroyed during the process of organification. A typical diffraction peak of ATT at 8.3° , which corresponds to a basal spacing of 1.04 nm, is evident according to Fig. 3. After

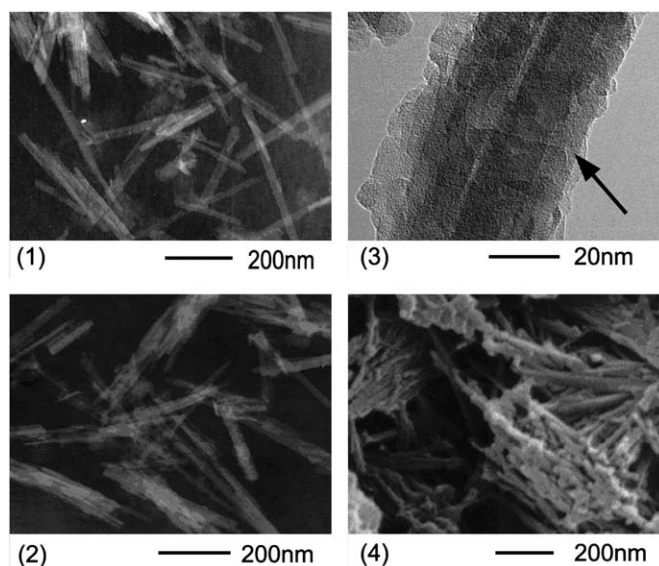


Fig. 5. The micrographs of (1) TEM image of ATT, (2) TEM image of BM-ATT, (3) HTEM image of BM-ATT, and (4) SEM image of BM-ATT.

organification, this peak appears also at 8.3° correspondingly. According to the results of XRD and FTIR, it can be concluded that all the reactions can just occur on the surface of ATT during the composite process without destroying the crystalline structure of it.

3.3. Thermal stability analysis

The amount of organics grafted onto ATT was determined using thermogravimetric analysis (TGA). The weight loss curves for ATT, M-ATT and BM-ATT are presented in Fig. 4. In the TGA curve (a), the weight losses at the range of 200 to 250°C are assigned to the release of the structure water of ATT. Because of being covered by the organics, M-ATT and BM-ATT are more thermally stable than the bare ATT below 300°C. The main weight losses starting at about 300°C are assigned to the thermal

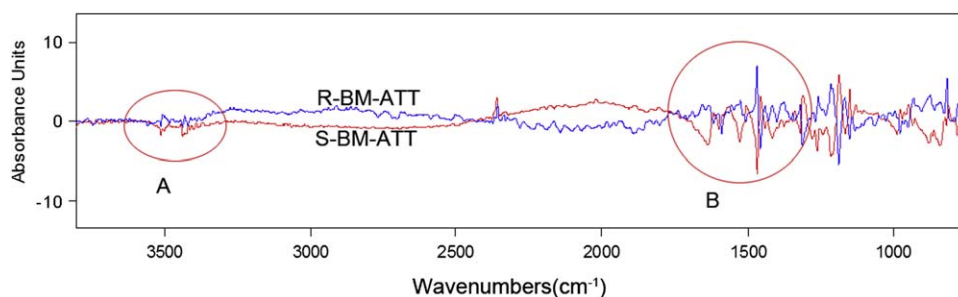


Fig. 6. VCD spectra of R-BM-ATT and S-BM-ATT.

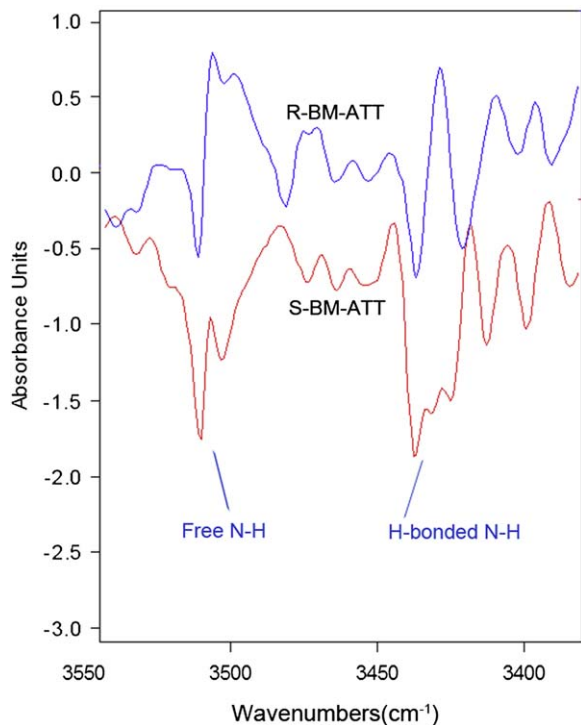


Fig. 7. VCD spectra of R-BM-ATT and S-BM-ATT from 3380 to 3550 cm^{-1} .

degradation of helical polyurethane for curve (c). TGA also indicates that the helical polyurethane has been successfully grafted onto the surfaces of the modified ATT.

3.4. Morphological analysis

Fig. 5(1) shows TEM image of ATT. It is clear that ATT exhibits a fibrous structure, and some fibers form straight parallel aggregates and rods. As can be seen in Fig. 5(2), after grafted with prepolymer based on R-BINOL, BM-ATT has similar rods structure and the parallel aggregates, however, the diameter of the rods is larger than that of bare ATT. Fig. 5(3) displays HTEM image of BM-ATT. As can be seen, the polymer wraps ATT rod (as denoted by arrow) firmly and the surface of composite is modified. SEM micrograph of BM-ATT was observed and is shown in Fig. 5(4). As can be seen in Fig. 5(4), BM-ATT shows rodlike fibrous nanoparticles with roughened surfaces coated by polymers. It could be included that ATT has been successfully modified by organification.

3.5. VCD spectra and optical activity analysis

Vibrational circular dichroism spectra can be applied to structural problems involving amino acids, peptides, and other natural optically active polymers, as well as chiral molecules of interest to organic or inorganic chemists. In order to investigate and compare the optical activity of BM-ATT based on R-BINOL, the BM-ATT based on S-1,1'-binaphthyl-2',2'-diol (S-BINOL) was prepared and called S-BM-ATT for short, compared with R-BM-ATT based on R-BINOL. VCD spectra of R-BM-ATT and S-BM-ATT are shown in Fig. 6. It is found that VCD signals of R-BM-ATT and S-BM-ATT display mirror image symmetry and obvious Cotton effect for some absorbance, although the grafted amount of polyurethane is only about 1.5 wt% (from TG curves). This result suggests that the grafted polyurethanes based on R-BINOL and S-BINOL are a couple of enantiomorphs and have the right-handed and left-handed rotation helical structures, respectively.

Fig. 7 is the amplificatory spectra of section (A) in Fig. 6. It is clear that the band at about 3500 cm^{-1} corresponding to the free N-H groups exhibit different absorptions. As can be seen, for R-BM-ATT, the band divides two opposite peaks, and there are two peaks downward for S-BM-ATT. That is because the free N-H groups are in the different chiral chemical environment, and R-BM-ATT and S-BM-ATT possess the optical activity resulting in Cotton effect. For the peaks at about 3425 cm^{-1} assigned to the hydrogen bonded N-H groups, the similar division is observed owing to the above reason.

Fig. 8 is the amplificatory VCD spectra of section (A) in Fig. 6 from 1050 to 1900 cm^{-1} . There is intense Cotton effect and wonderful mirror image symmetry between R-BM-ATT and S-BM-ATT in Fig. 8. The bands at about 1610, 1545, and 1510 cm^{-1} , assigned to C=O, amide I and amide II, respectively, exhibit different absorptions. The opposite Cotton effect indicates that R-BM-ATT and S-BM-ATT possess symmetrical helical conformations. On the basis of above analysis, it is found that R(S)-BM-ATT with rod-like structure is coated by optically active shell resulting from the helical conformation.

4. Conclusions

Helical polyurethane@attapulgit nanocomposite was prepared successfully after the surface modification of ATT by MDI. The helical polyurethane has been grafted onto the surfaces of the modified ATT without destroying the original crystalline structure of ATT. BM-ATT exhibits rod-like structure coated by optically active shell. BM-ATT displays obvious Cotton effect for some absorbance in VCD spectrum. The optical activity of BM-ATT is deriving from singlehanded conformation of helical polyurethane.

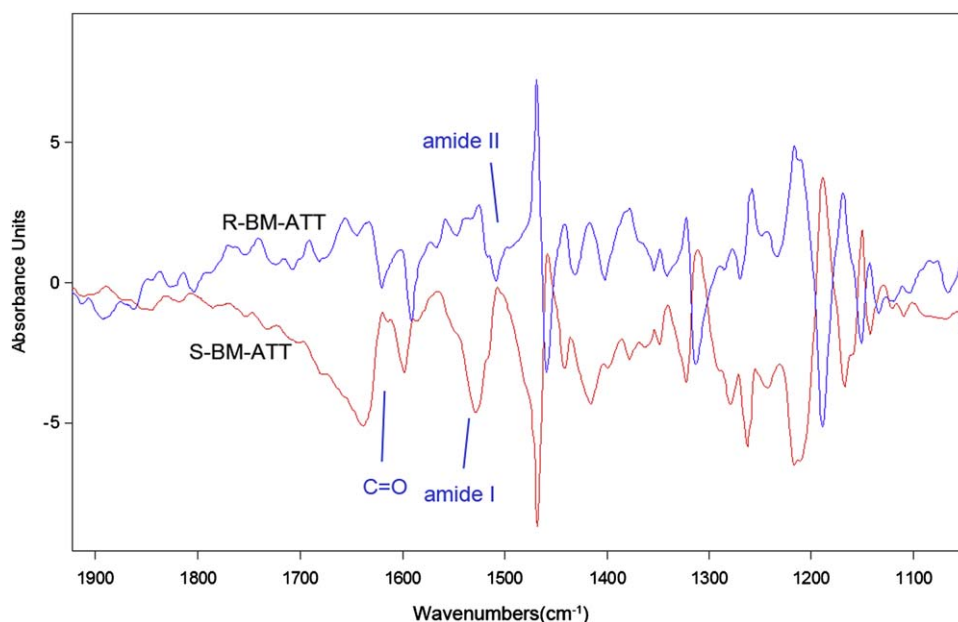


Fig. 8. VCD spectra of R-BM-ATT and S-BM-ATT from 1050 to 1900 cm^{-1} .

Acknowledgments

The authors are grateful to the National Nature Science Foundation of China (50873026), Science and Technology Support Program of Jiangsu Province of China (BE2008129), Six Talents Pinnacle Program of Jiangsu Province of China (06-A-033) for financial supports and Excellent Doctoral Thesis Foundation of Southeast University.

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