論文 / 著書情報
Article / Book Information

題目(和文)	ブロック共重合体を鋳型 用いる周期性メソポーラスポリイミド膜及びカーボンの創製
Title(English)	Preparation of Ordered Mesoporous Polyimide Films and Carbons via Block Copolymer Templating
著者(和文)	GaoLing
Author(English)	Ling Gao
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10765号, 授与年月日:2018年3月26日, 学位の種別:課程博士, 審査員:早川 晃鏡,芹澤 武,石曽根 隆,戸木田 雅利,道信 剛志
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10765号, Conferred date:2018/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	有機・高分子物質　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
学生氏名： Student's Name	高凌（Ling GAO）	指導教員（主）： Academic Supervisor(main)	早川晃鏡
		指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

To obtain well-ordered mesoporous polymer film and carbon via block copolymer template-assisted approach is the central purpose of this research. The key focus is on fabricating new materials with ordered mesoporous and desired properties in films and carbons by combining N-containg polymeric precursor and soft template. Compared with the mesoporous polymers prepared from phenolic resin precursors and olefin type BCPs, wholly aromatic polymers with high performance capabilities and ordered mesoporous structures are more attractive in nanotechnology and electrochemistry. In the previous work about the preparation of porous polyimides, there remained a challenge in obtaining ordered mesoporous polyimide with narrow pore size distributions for further application. In this study, mesoporous polyimide bulk, thin, and carbon films were successfully obtained via amphiphilic BCP template methods.

Chapter 2**,** a system based on the F127/AA/R was introduced to obtain well-ordered mesoporous carbons via high-temperature carbonization. Well-ordered NMCs with hexagonally arranged, uniform, ~4 nm mesopores and defects in the graphitic carbon lattice were successfully synthesized. Elemental analysis revealed that the nitrogen content decreased from approximately 2 to 0.3 wt% in both the NMC-T and NT-T samples after heat treatment from 900 to 1500 °C. This could be attributed to the N-atom removal mechanism that occurs in NMCs heated above 1100 °C. The obtained NMCs with highly ordered mesoporosity (pore size is ~ 4.2 nm), narrow pore size distribution, high surface areas (500-600 m^2g^{-1}), and defect-inclusive graphitized carbons are promising for highly advanced functional applications.

Chapter 3**,** PS-*b*-PMAA was used as the template to self-assemble with the wholly aromatic PAA to form nanostructure in as-prepared PAA films. The PAA with flexible structure shows good compatibility with the PS-*b*-PMAA template both in bulk and thin films. This is attributed to the hydroxyl groups in PAA that can interact with PMAA block of PS-*b*-PMAA through hydrogen bonding to form hydrophilic domain that can self-assemble with PS domain. SAXS analysis revealed that the ordered lamellae structures were obtained in the as-prepared PAA bulk film. After the thermal decomposition of the PS-*b*-PMAA template, the nanostructure was collapsed in polyimide film due to the imidization of PAA and simultaneously mobility of PS. On the other hand, the well-ordered nanostructures were observed in PAA thin film. However, the structure was collapsed during thermal imidization. To further stabilize the ordered structure, an alternative way to decompose minor block of

BCPs to form pores under low temperature is necessary.

Chapter 4**,** PαMS-*b*-PMAA and PAA were blended in DMF and well-defined spherical nanostructures were also obtained in composite polymer films. Compared with PS-*b*-PMAA, the introducing of a UV degradable PαMS block offers an alternative way to form porous structure besides thermal decomposition. After the thermal treatment of a PαMS-*b*-PMAA/PAA/R 40:40:20(w/w) sample, SAXS, and SEM confirmed the existence of spherical mesoporous structures in polyimide films. On the other hand, the ordered dot structures observed in PAA thin films were collapsed during PαMS removal by UV decomposition. It is considered due to the limited cross-linked network that can not retain the ordered structure.

Chapter 5**,** PαMS-*b*-PHOST, which consists of a UV degradable block and cross-linkable block, self-assembled with PAA in DMF to form spherical nanostructure in PAA film were obtained. For PαMS-*b*-PHOST/PAA/R 40:40:20(w/w) bulk sample, well-defined spherical mesoporous polyimide film by thermal decomposition. For PαMS-*b*-PHOST/PAA/R 40:40:20(w/w) thin sample, well-defined spherical mesoporous structure was obtained by thermal UV decomposition. The BCP likely cross-linked with resol, due to a similar phenolic structure of resol and PHOST in PαMS-*b*-PHOST, allowing for cross-linking with resol and the formation of a stable network during imidization. Moreover, the spherical mesoporous carbon film was retained after heat treatment of the polyimide at 900 °C in an inert atmosphere for 1 h.

Functionalized well-ordered mesoporous carbons with structural defects were obtained. Furthermore, novel various BCPs were successfully designed as template for preparation of well-defined mesoproosu polyimide film and carbons. Properly chosen of block copolymer and functional polymer precursor with optimized solvent condition, it is highly possible to obtain ordered mesoporous high properties polymer via block copolymer template-assisted approach that broad its thermal and electrical application.