

Mesoporous Carbons from Poly(acrylonitrile)-b-Poly(ϵ -caprolactone) Block Copolymers

A series of degradable block copolymers, poly(acrylonitrile)-b-poly(ϵ -caprolactone) (PAN-PCL), have been synthesized by sequential living polymerization in this study. Well-defined, microphase-separated PANPCL microdomains can be efficiently achieved in the bulk by using appropriate solvents. The microphase-separated lamellar samples were then used as templates to produce mesoporous carbons at which large amounts of porous texture in carbonized PAN matrix were formed after degradation of PCL due to randomly oriented lamellar texture (namely, interconnection of PCL microdomains). The thermal profiles for efficient stabilization were examined by differential scanning calorimetry and thermogravimetric analyses as well as Fourier transform infrared spectroscopy. Consequently, mesoporous carbon materials might be prepared as evidenced by transmission electron microscopy, field emission scanning electron microscopy, and small-angle X-ray scattering. The formation of carbonized materials was identified in accordance with the presence of carbon diffractions by wide-angle X-ray diffraction. In contrast to the thermal stability of the carbonization of PAN homopolymers, it is noted that the carbonization procedure can be achieved in the PAN-PCL system regardless of the stretching process (that is an essential process to improve the thermal stability of PAN carbonization). We speculate that this unique feature for the carbonization of PAN copolymers might be attributed to the stretched chains of PAN under nanoscale confined environment.



The objective of this study is the manufacture of mesoporous carbons via carbonization of microphase-separated PAN containing block copolymers with degradable character. Block copolymers containing aliphatic polyesters draw extensive attention in the preparation of mesoporous polymers attributed to the ease degradation of ester groups.¹⁻³ Herein, we report a synthetic strategy to fabricate mesoporous carbon materials with graphite-like network structure through self-assembled block copolymers in which the carbon precursor (PAN) is preorganized into well-defined nanostructures (e.g., cubic, cylinder, lamellae) induced by the presence of degradable block (i.e., poly(ϵ -caprolactone) (PCL)) which could be removed by pyrolysis or hydrolysis. Also, we found that the carbonization procedure can be achieved in the PAN-PCL system regardless of the stretching process (that is an essential process to improve the thermal stability of PAN carbonization). Consequently, this approach may provide a satisfactory addition to the methods for the manufacturing of mesoporous carbons from PAN containing block copolymers and a new way for PAN carbonization by taking advantage of microphase separation.

Beamline

17B3 Small Angle X-ray Scattering

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To identify the morphology of PAN-PCL, microsections of quenched PAN-PCL samples (referred as pristine samples) were examined by TEM. Owing to the RuO₄ staining effect, PAN and PCL microdomains appeared as dark and bright regions, respectively. As observed, the TEM image of AN05CL03 ($f_{\text{PAN}}^v = 0.6$) (Figure 1a) exhibited typical microphase-separated lamellar morphology. Corresponding SAXS results (Figure 1b) further confirm the observed lamellar nanostructure where the scattering peaks occur at q^* ratio of 1:2 and the d-spacing is determined as 16 nm. The broad second peak is attributed to the PCL crystalline leading to much significant electron density variation from PAN and amorphous PCL. Consequently, the broadness of the peak becomes narrow as examined at temperature above T_m of PCL blocks (dotted line of Figure 1b).

One indispensable process for carbonization of PAN is stabilization, a process well-known in the field of carbon fibers, achieved through specific thermal treatment. The stabilization process of PAN precursor fibers involves low-temperature heating (200–300 °C) of the fiber to transform them into a structure that can be subjected to high-temperature carbonization treatment without melting or fusion of the fibers. The unsaturated side groups (nitrile groups) in the linear polymer of PAN undergo a polymerization reaction on heating, then form a cyclized structure known as a ladder structure, and finally become a cross-linked network. The cyclized structure is stable toward heat and can be converted to turbostratic carbon on subsequent carbonization at high temperatures (~1000–2000 °C) in an inert atmosphere (i.e., in nitrogen atmosphere) or vacuum.^{4,5} The pristine samples were heated at 230 °C for 20 hrs in atmosphere for stabilization. The morphology was thus examined by TEM and SAXS. As

shown (Figure 2a), the samples retain the intrinsic nanostructure even though the d-spacing becomes larger (c.a. 17 nm). The preserved nanostructure was further identified by SAXS (Figure 2b) where the scattering peaks were found to occur at q^* ratio of 1:2, and the d-spacing was determined as 20 nm from the primary peak, good agreement with the TEM results. The domain spacing increased from 16 to 20 nm according to the SAXS results, whereas the domain spacing increased from 14 to 17 nm as observed by TEM. The expected change might be attributed to the formation of ladder structure resulting from chain stretching during stabilization.⁶

To complete the carbonization procedure, the stabilized samples were further heated to 800 °C. The progress of carbonization of PAN block copolymer was monitored with SAXS and WAXD. While at high-temperature thermal treatment, a broad bump in the SAXS profile (Figure 3a) could be clearly identified. The diffused scattering result might be attributed to the formation of large amounts of random-oriented pores. Figure 3b is the comparison of WAXD profiles observed for pristine, stabilized and carbonized samples at room temperature from $2\theta = 10^\circ$ to 40° . The main reflection of pristine PAN-PCL in the WAXD pattern was at $2\theta = 16.7^\circ$, corresponding to PAN which was similar to PAN fiber precursor, and a weak reflection at $2\theta = 29^\circ$ as well.⁷ PCL blocks showed two strong reflections at $2\theta = 21.3$ and 23.6° . Upon stabilization, the reflections of PAN component at $2\theta = 16.7^\circ$ and 29° became sharper and stronger due to the improvement in the orientation under dimensional constraints so as to lead the perfection of the molecular chain packing. Also, the reflections of crystalline PCL blocks disappeared in the profile of stabilized PAN-PCL due to some thermal degradation at such high temperature, even though PCL blocks had not been thermal degraded completely. After carbonization, a broad peak centered at $2\theta = 25.8^\circ$, which corresponded to the interplanar spacing of 0.36 nm, developed. The peaks could be identified as (002) spacing of a graphitic carbon structure. From the results, carbonized PAN-PCL block copolymer had a graphite-like carbon structure.

PAN-PCL is a new nanocarbon precursor system in which PAN block is the carbonization precursor and PCL block is the degradable component. The nanostructures of PAN-PCLs were

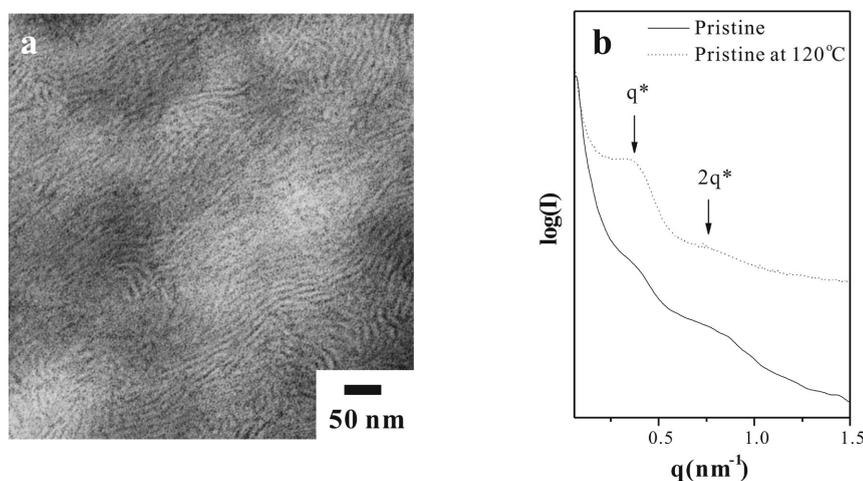


Fig. 1: (a) TEM micrograph of pristine AN05CL03 ($f_{\text{PAN}}^v = 0.6$) and (b) corresponding 1D SAXS profiles examined at room temperature and 120 °C.

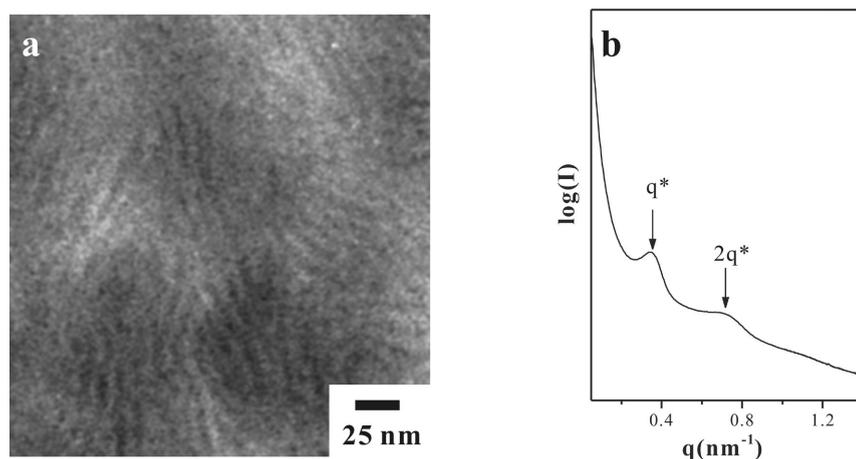


Fig. 2: (a) TEM micrograph and (b) 1D SAXS profile of stabilized AN05CL03. The stabilized samples were heated at 230°C for 20 hrs in atmosphere.

identified by TEM and SAXS results. The stabilization condition of PAN block copolymer was identified by thermal analysis, and the stabilized nanostructure was identical to intrinsic texture. PCL blocks can be thermally degraded without involving the change on nanostructure. In contrast to the preservation of nanostructure after thermal degradation of PCL, the hydrolytic process for PCL component may cause the change of intrinsic nanostructures due to the simultaneous etching of PAN and PCL components during hydrolysis. Systematic study with respect to the achievement of optimal condition for hydrolysis should be carried out in order to preserve the templated nanostructure after hydrolysis. Also, significant change on the self-assembled nanostructures was found after carbonization at which the templated nanostructures may vary due to the collapse of mesoporous matrix. We thus expect that the mesoporous carbon scaffolds can thus be manufactured from carbonization of bulk PAN templates once optimal conditions for carbonization can be achieved. Consequently, the self-assembly PAN-PCL materials may give rise to a promising and convenient way for the manufacturing of mesoporous carbons.

Publication

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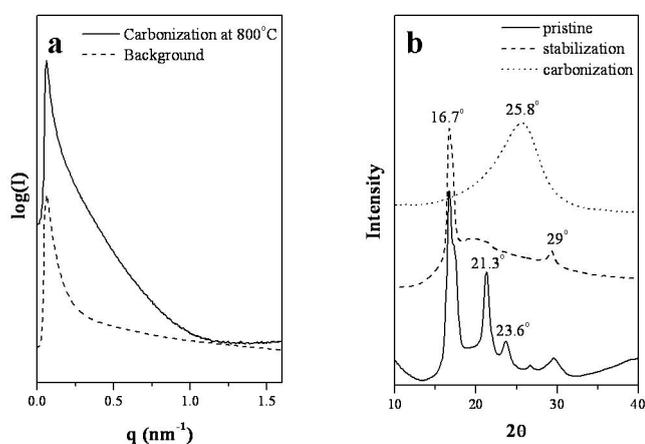


Fig. 3: (a) SAXS profiles of carbonized AN05CL03 and background. (b) WAXD profiles of each step of carbonization procedure.