

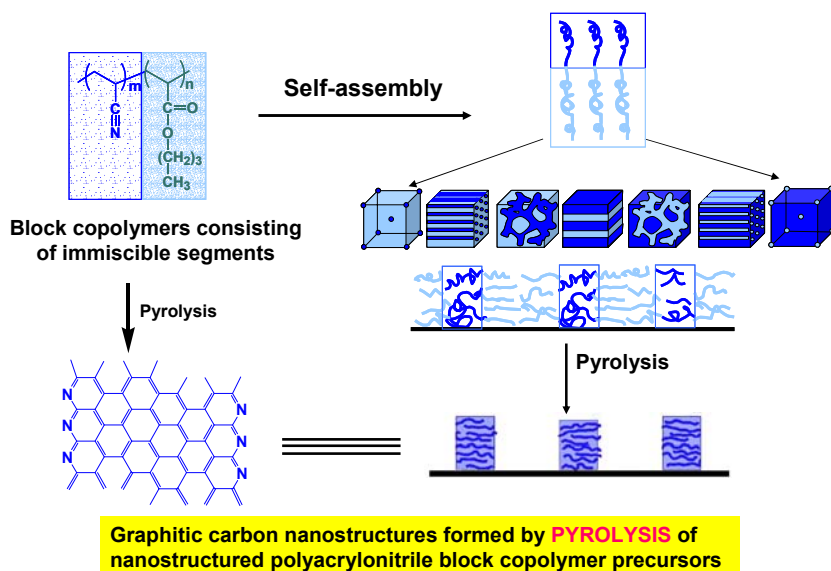
Morphology and Thermal Behavior of Well-Defined Polyacrylonitrile-*b*-Poly(*n*-butyl acrylate) Block Copolymer Precursors for Nanostructured Carbons

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Introduction

This study is motivated by our recent discovery that block copolymers containing polyacrylonitrile (PAN) can be converted through pyrolysis into carbon materials with well defined nanostructure, templated after the phase-separated nanostructures of a block copolymer (Scheme 1).^[1, 2] The key to the preservation of original copolymer nanostructure in this process is a thermal stabilization step, in which material is subjected to heat treatment in the presence of air. This thermal stabilization process is well known (although still not fully understood) in the field of carbon fiber manufacturing,^[3] in which PAN has played an important commercial role as carbon precursor. Herein we are presenting an attempt to elucidate its progress in well-defined block copolymers of PAN with poly(*n*-butyl acrylate) (PBA). More detailed knowledge of thermal stabilization in these systems is necessary to optimize their conversion into nanostructured carbons.



Applications: electronic devices such as field emitters; photovoltaic cells; supercapacitors

Scheme 1 Preparation of nanostructured carbon by pyrolysis of PBA-*b*-PAN block copolymer precursors

Synthesis of well-defined block copolymers of PAN^[4-7] is a recent development spurred by the progress in the field of controlled radical polymerization processes such as atom transfer radical polymerization (ATRP^[8]), reverse addition chain fragmentation transfer polymerization (RAFT^[9]) and nitroxide mediated polymerization (NMP^[10]). Two major stages in the process in which PAN block copolymers are converted into nanostructured carbons are: (1) cross-linking and some cyclization of PAN microphase through heating in the temperature range from 200 °C to 300 °C in oxidative environments, and (2) further cyclization followed by dehydrogenation, denitrogenation and conversion to partially graphitic structures, upon continued heating to higher temperatures under inert atmosphere. In step (1), in analogy with the process used for stabilization of carbon fibers, PAN microphase undergoes cross-linking and some cyclization, which prevents homogenization above the order-disorder transition temperature. Step (2) leads to almost complete carbonization of PAN and decomposition and volatilization of the sacrificial block (PBA).

In order to elucidate the transformation of PAN copolymers upon thermal treatment, the glass transition,^[11] stabilization/oxidation, decomposition and carbonization^[12] behavior of these novel block copolymers were studied with the aid of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The PAN content in the precursors used in the current study ranged from 3.6 wt% to 55.4 wt%, spanning the compositions from those yielding highly dispersed PAN domain structures to those resulting in materials with continuous PAN matrix.^[13]

Experimental

PBA-*b*-PAN block copolymer precursors were prepared as described earlier.^[6] Compositions and morphologies of copolymers used in this study are listed in Table 1. Thin film samples were prepared by drop-casting a 10 mg/mL copolymer solution in DMF onto cleaned silicon wafer substrates and vacuum drying. Nanoscale morphologies were characterized by tapping mode atomic force microscopy (TMAFM) with the aid of a NanoScope III-M system (Digital Instruments, Santa Barbara, CA), equipped with the J-type vertical engage scanner. The AFM observations were performed at room temperature in air using silicon cantilevers with nominal spring constant of 40 N/m and nominal resonance frequency of 300 kHz (standard silicon TESP probes). Thermal characterization of bulk samples (6-14 mg) was carried out with the aid of Seiko DSC 220 and Seiko TGA/DTA 300 instruments (Seiko Instruments, Inc.) operated at the heating rate 10 °C/min under controlled atmosphere (air, N₂, O₂, flow rate 30-60 mL/min).

Results and Discussion

The characteristic phase separation of diblock copolymers is dictated by the Flory-Huggins parameter χ , total degree of polymerization and composition f .^[14] Classical phase diagram of amorphous random-coil block copolymers is represented by symmetrical distribution of nanostructures on the composition. In the case of copolymers containing PAN, the phase diagram can be significantly modified due to the

tendency of PAN molecules to adopt a stiff, rod-like, irregular helical structure under the influence of *intramolecular* dipole repulsion between nitrile groups.^[15] Moreover, the *intermolecular* dipole attraction tends to pack the helices into laterally ordered

Sample Code	Composition (DP _{BA} /DP _{AN})	M_w/M_n	w%(AN)	Tentative Morphology
D-38	202/18	1.17	3.6	<i>Disordered</i>
D-2	360/41	1.15	4.6	<i>Spherical</i>
D-11	240/38	1.23	5.8	<i>Spherical</i>
D-36	202/55	1.25	9.7	<i>Spherical</i>
D-8	250/69	1.18	10.3	<i>Spherical/Cylindrical</i>
D-7	250/86	1.16	12.5	<i>Spherical/Cylindrical</i>
D-10	240/100	1.23	15.7	<i>Cylindrical</i>
D-6	250/130	1.25	17.7	<i>Cylindrical/Lamellar</i>
D-34	202/107	1.30	17.9	<i>Lamellar</i>
D-9	240/129	1.22	18.2	<i>Lamellar/Gyroid</i>
D-12	250/148	1.34	18.5	<i>Lamellar</i>
D-40	141/128	1.36	26.8	<i>Lamellar</i>
D-39	78/112	1.36	38.3	<i>Reversed Gyroid</i>
D-41	40/112	1.32	55.4	<i>Reversed Spherical/Cylindrical</i>

Table 1. Molecular weight and morphology of PBA-*b*-PAN block copolymers (DP = degree of polymerization)

domains.^[15] Thus, although lack of tacticity would imply inability of PAN to crystallize, it has certain characteristics of a semicrystalline polymer.^[15] Such significant modifications of phase diagram in comparison with "classical" random-coil copolymer systems have been indeed observed in our recent study of nanoscale morphology of PAN copolymers.^[13]

Its most pronounced manifestation is the fact that lamellar morphologies, which in "classical" systems are observed at approximately equal fractions of both blocks, occur in PAN diblocks at PAN contents as low as ~ 25 w% (Figure 1). The central question posed by this study is the relationship between the nanoscale morphology of PAN copolymers and their thermal behavior, with particular emphasis on cyclization processes, which are critical for the survival of these morphologies upon carbonization.

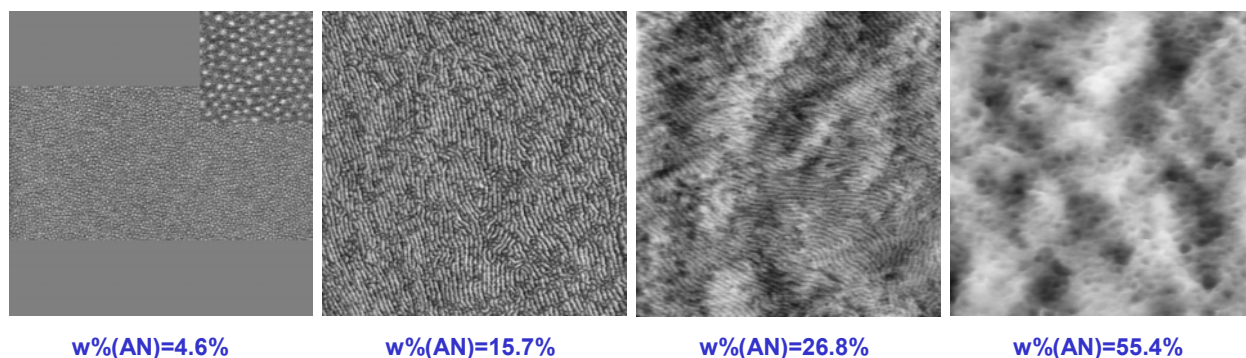


Figure 1. AFM images of various nanostructures of PBA-*b*-PAN block copolymers with increase of PAN composition from the left to the right. Image size 3 x 3 μm .

The DSC traces of all copolymers (Figure 2) exhibited pronounced features around -45 $^{\circ}\text{C}$ corresponding to the glass transition (devitrification) of PBA and less prominent (but consistently reproducible) features corresponding to devitrification of PAN. Devitrification of PAN in copolymers exhibited quite complex dependence on thermal history of the material. In the case of materials with high PAN content (e.g. D41 and D39), the glass transition feature around 95 $^{\circ}\text{C}$ was well defined, it was much less distinct in the second and third runs. With the decrease of PAN content, the devitrification transition was still observable although less pronounced.

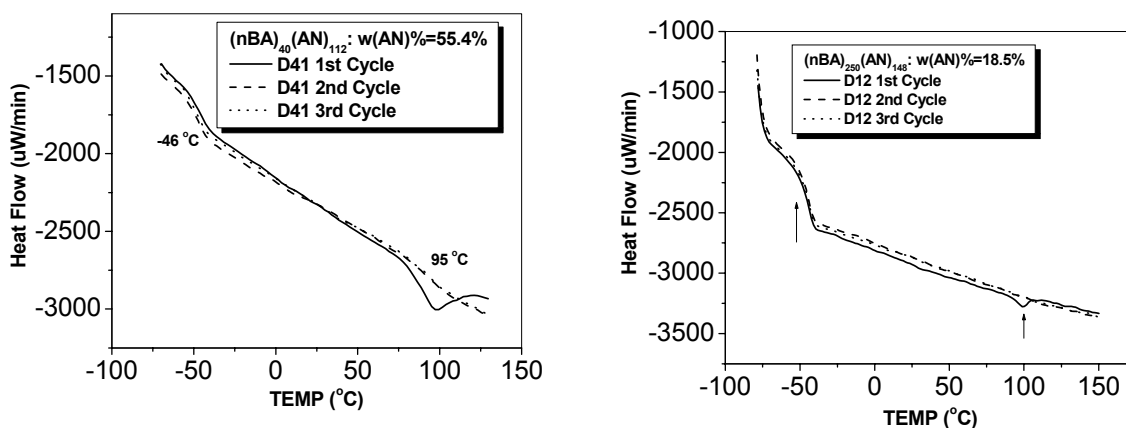


Figure 2. DSC traces showing the glass transitions of PBA and PAN in PBA-*b*-PAN block copolymers: (Left) D41; (Right) D12

DSC studies provided also information about the stabilization/oxidation of PAN and decomposition of PBA. Transitions corresponding to these processes were manifested in all DSC traces (Figure 3) respectively as sharp exotherms (peak position: ~ 280 - 300 $^{\circ}\text{C}$; range: ~ 220 - 330 $^{\circ}\text{C}$) and endotherms (peak position: ~ 390 - 405 $^{\circ}\text{C}$; range: ~ 350 - 430 $^{\circ}\text{C}$). While the peak position in the exotherms corresponding to cyclization did not exhibit systematic dependence on composition, the onset of exotherms shifted to lower temperature and the exotherms became broader for lower PAN content, possibly

pointing to the role of interfacial effects. In contrast, the position of endotherms corresponding to the decomposition of PBA did not appear to be affected by copolymer composition. Moreover, in all cases the exotherms were well separated from endotherms. Such behavior is highly desirable in our system, since PBA is supposed to play the auxiliary role as a sacrificial block, minimally interfering with cyclization and pyrolysis of PAN domains.

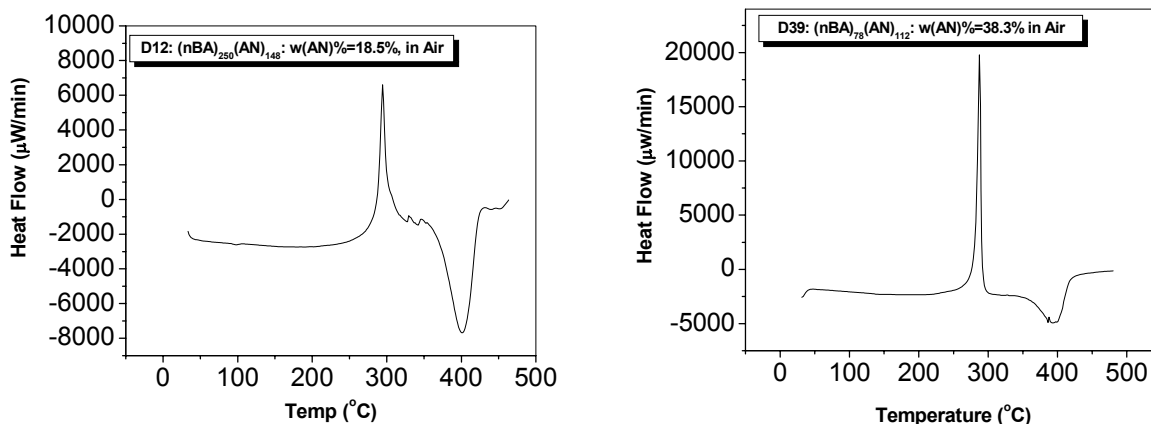


Figure 3. DSC traces showing the stabilization/oxidation exotherms of PAN block and decomposition endotherms of PBA block in PBA-*b*-PAN block copolymers: (Left) D12; (Right) D39

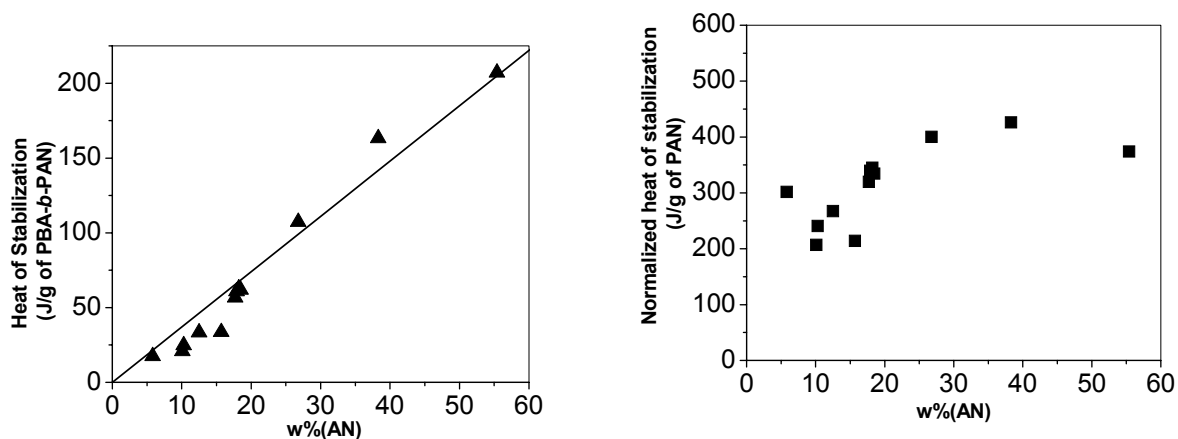


Figure 4. The dependence stabilization exotherm area on PAN content in PBA-*b*-PAN block copolymers: (Left) Exotherm area normalized to the total copolymer mass; (Right) Exotherm area normalized to the mass of PAN block

As expected, the area under the cyclization exotherms normalized to the mass of a copolymer exhibited approximately linear dependence on weight fraction of PAN (Figure

4, left). However, more detailed analysis in which the area normalized to weight fraction of PAN was plotted (Figure 4, right) showed that the overall heat of cyclization was lower for materials with PAN content below ~ 25 w%. Such behavior can be well understood given the fact that materials in this composition range form highly dispersed morphologies with PAN domains characterized by high surface to volume ratios.

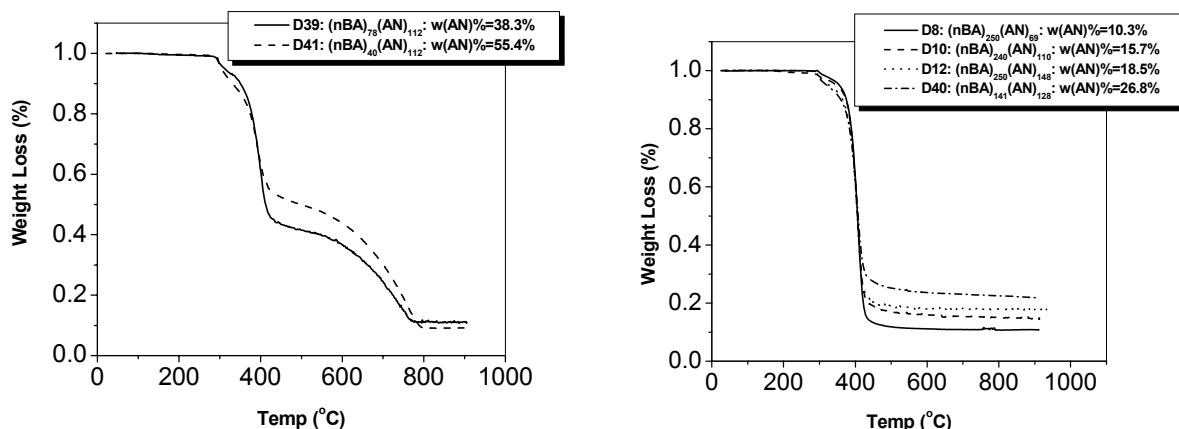


Figure 5. Weight loss curves of PBA-*b*-PAN block copolymers upon heating in N₂ atmosphere for materials with high (left) and low (right) PAN content.

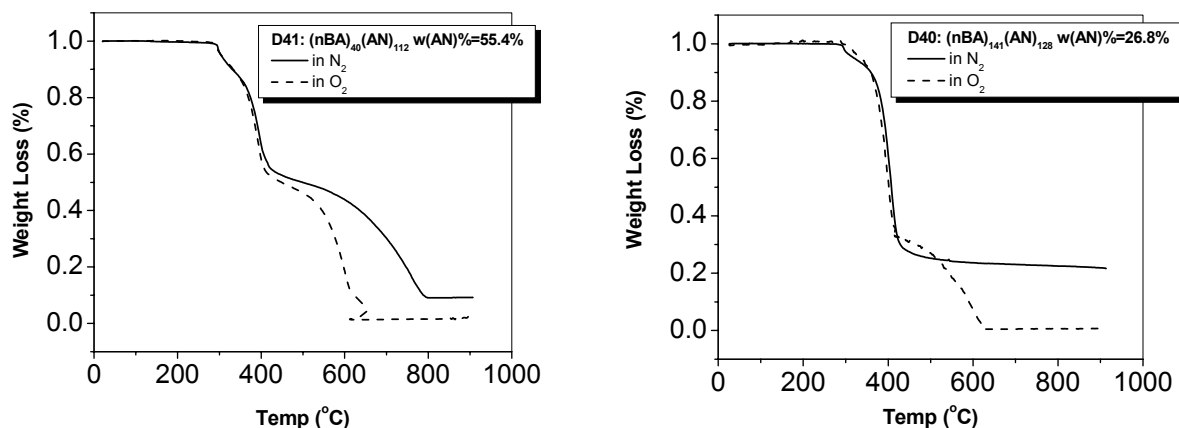


Figure 6. Comparison of weight loss exhibited by PBA-*b*-PAN block copolymers with high (left) and low (right) PAN content upon heating in N₂ and O₂ atmosphere.

Comprehensive TGA characterization was mainly carried out under inert (N₂) atmosphere with a few experiments under oxidative conditions (O₂ and air). All weight loss curves exhibited three stages corresponding to: (1) stabilization/oxidation, (2) decomposition and (3) carbonization (Figure 5). Up to ~ 230 °C, all materials exhibited virtually no weight loss. A slight weight loss (1) between 230 - 340 °C can be attributed

to the stabilization/oxidation reaction of PAN. A significant weight loss in the step (2) between 350-430 °C, is obviously associated with the decomposition of PBA, occurring in the range similar to that observed for PBA homopolymer (not shown). Temperature ranges for steps (1) and (2) determined by TGA are in good agreement with those observed by DSC. Of particular interest are observations related to the weight loss in the temperature range 450 °C- 900 °C corresponding to step (3). Whereas materials with PAN content above ~35 wt. % exhibited significant weight loss in this range (just like PAN homopolymer), copolymers with lower PAN content exhibited here minimal weight loss. This results points to the intriguing possibility that thermal stabilization is more efficient in materials with highly-dispersed PAN domains, presumably due to their better accessibility to oxygen. Under the oxidative atmosphere (O₂), up to 500 °C the weight loss of block copolymers was similar to one observed in inert atmosphere, however at higher temperatures all materials effectively burnt away (Figure 6), pointing to the critical importance of maintaining inert atmosphere upon pyrolysis.

PBA-*b*-PAN block copolymers prepared by nitroxide-mediated polymerizations (D9, D10 and D11, not shown) showed similar thermal behavior to their counterparts prepared by ATRP. This is a significant observation, which indicates that lability of nitroxides does not lead to thermal destabilization of these copolymers, probably due to high ceiling temperatures of PBA and PAN blocks.

Conclusions

In summary, our studies revealed that the extent of stabilization and therefore further carbonization of PBA-*b*-PAN block copolymers is strongly dependent on copolymer morphology and in particular on the PAN domain surface-to-volume ratio. Materials with dispersed PAN domains can be more efficiently stabilized than those with continuous PAN domains. The insights obtained in this study open the way to optimization of the thermal treatment of PAN copolymers necessary to prepare high quality nanostructured carbons. Nanostructured carbons prepared using our approach are expected to find many applications, e.g., as materials for field emitters, specialized electrodes, sensors, etc.

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