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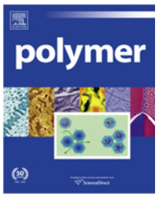

Design of mesoporous carbon fibers from a poly(acrylonitrile) based block copolymer by a simple templating compression moulding process

Jean-Michel Thomassin, Antoine Debuigne, Christine Jérôme, Christophe Detrembleur*

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman B6a, 4000 Liège, Belgium

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ABSTRACT

Mesoporous carbon fibers were prepared by controlled pyrolysis of poly(vinyl acetate)-*b*-poly(acrylonitrile) (PVAc-*b*-PAN) copolymer located inside a cylindrical nanoporous template. A melt-compression method was developed to help the penetration of the infusible copolymer inside the template without the use of any solvent that ensures the formation of completely filled fibers instead of nanotubes. The influence of the composition of the PVAc-*b*-PAN copolymer and the heating rate during pyrolysis on the porous morphology of the fibers was studied by transmission electron microscopy (TEM).

1. Introduction

Carbonaceous materials prepared by pyrolysis of organic molecules have been widely used in many areas of chemistry and chemical engineering such as catalysis [1,2], sensors [3], electrode materials for cells [2,4], gas storage [5] and purification [6]. These applications generally require carbon materials with a high surface area which justifies the intensive researches focused on the maximization of this property by controlling the pores size and their distribution in the materials. For this purpose, two main strategies can be distinguished. The first one consists in the decrease of the carbon particles size which led to the preparation of fullerene [7], carbon nanotubes [8] and individual carbon sheets [9]. The second method relies on the formation of highly porous carbon materials with small interconnected pores. These materials can be classified as microporous (<2 nm), mesoporous (2–50 nm) and macroporous (>50 nm) depending on the pore size [10]. These materials are generally prepared using a porous template such as silica that is filled with an organic precursor [11–14]. After carbonization of the precursor, the silica is removed by treatment with hydrofluoric acid or concentrated alkali. The organic precursors are generally based on polymers such as polyacrylonitrile, polyimide, polybenzimidazole, cellulose… Another method is based on the use of block copolymers or phase separated blends where one component consists in the previously mentioned organic precursor and the other component plays the role of a sacrificial part that creates the pore structure during pyrolysis [15–26]. Small films are generally used as starting materials but the current tendency is to use materials that already develop a high surface area such as fibers. These fibers are mostly prepared by electrospinning of polyacrylonitrile based block copolymer or blends solutions [10,27–29]. However, this technique results in the formation of a highly interpenetrated network where the fibers are difficult to disentangle. In order to avoid such problem, Russel et al. filled anodic aluminum oxide (AAO) nanotemplates with PAN containing block copolymer solutions to prepare carbon nanotubes [30]. In this process, the cylindrical pores of the nanotemplate are filled by a solution of the poly(styrene)-*b*-poly(acrylonitrile) (PS-*b*-PAN) block copolymer. During solvent evaporation, the polymer deposits on the template surface leaving the center of the cylindrical pores empty. Graphitization at a temperature of 600 °C then leads to carbon nanotubes after dissolving the template. This technique has the advantage that the nanotubes are not entangled during the formation process.

In our study, we develop a templating compression moulding process for preparing mesoporous carbon fibers instead of carbon nanotubes using a poly(vinyl acetate)-*b*-poly(acrylonitrile) (PVAc-*b*-PAN) block copolymer, the PVAc block being the sacrificial block while PAN is the carbon precursor. In this process, an anodic aluminum oxide (AAO) membrane is used as the template but the penetration of the block copolymer is forced by pressing the

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* Corresponding author.
E-mail address: christophe.detrembleur@ulg.ac.be (C. Detrembleur).

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Table 1
Molecular characteristics of the three copolymers used in this study.

Name (weight ratio)	Mn	PDI
PVAc-*b*-PAN 80/20	21 500–5500	1.48
PVAc-*b*-PAN 55/45	23 500–19 000	1.22
PVAc-*b*-PAN 36/64	29 500–54 000	1.29

molten copolymer on the template. The whole pores are consequently completely filled by the copolymer. This technique has been widely used for classical block copolymers (such as poly(styrene)-*b*-poly(butadiene) [31,32], poly(styrene)-*b*-poly(methyl methacrylate) [33], poly(styrene)-*b*-poly(ethylene oxide) [34] and poly(styrene)-*b*-poly(2-vinylpyridine) [35]) by simply depositing an AAO template on the top of a molten copolymer film. The strong capillary forces drew the copolymer inside the nanopores of the template. However, our carbon precursor block (poly(acrylonitrile)) of the copolymer is infusible which prevents the use of this method. We therefore develop a compression moulding process to force the copolymer to enter the template. The second block has a dual role of (i) favoring the penetration of the block copolymer inside the nanopores of the template, thanks to its low Tg, and (ii) creating the nanopores in the final carbon fibers by pyrolysis and volatilization at high temperature. The influence of the PAN/PVAc ratio and the heating rate during pyrolysis on the porous morphology of the fibers was studied by transmission electron microscopy (TEM).

2. Experimental part

2.1. Materials

The AAO membranes (thickness 60 μm, pore diameter 150–400 nm) were purchased from Whatman Ltd. PVAc-*b*-PAN block copolymers are prepared by cobalt-mediated radical polymerization (CMRP) [36] according to a previously reported procedure [36,37]. Molecular characteristics of the copolymers are summarized in Table 1.

2.2. Carbon fibers preparation

The procedure used for the preparation of mesoporous carbon fibers is represented in Fig. 1. Films of PVAc-*b*-PAN (thickness = 100 μm) are first prepared by compression moulding at 180 °C under 80 bar. An AAO membrane is then placed on the top of these films and a pressure of 80 bar is applied at 180 °C for 10 min. The filled AAO membranes are then placed in a Hi-Res TGA Q500 from TA Instruments for thermal treatment. The structure is first stabilized with a treatment at 240 °C for 1 h under air, before increasing the temperature to 600 °C using different heating rates (20, 5 and 1 °C/min) under nitrogen. The AAO template was then dissolved with a 5 wt% NaOH solution for 2 h. The tubes were then collected using an ultrasonic treatment and repeatedly washed with water.

2.3. Characterizations

Fiber morphologies were observed by scanning electron microscopy (SEM; JEOL JSM 840-A) after metallization with Pt (30 nm) and by transmission electron microscopy (FEI, TECNAI G2 TWIN) at an accelerating voltage of 200 kV. Image analysis was performed manually by measuring the size of at least 300 pores on the basis of SEM pictures.

3. Results and discussion

Fibers of poly(vinyl acetate)-*b*-poly(acrylonitrile) (PVAc-*b*-PAN) block copolymers were prepared by template wetting of anodic aluminum oxide (AAO) membranes with cylindrical pores as depicted in Fig. 1. The use of solvent has been avoided since it leads to the formation of nanotubes instead of completely filled fibers [30].

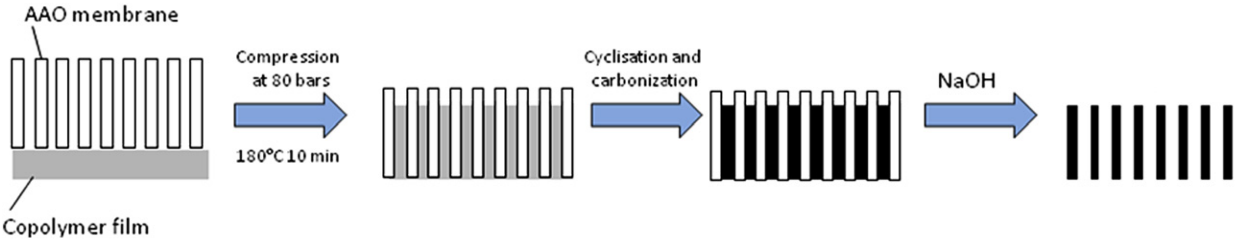

Fig. 1. Schematic diagram of the procedure used for the preparation of mesoporous fibers.

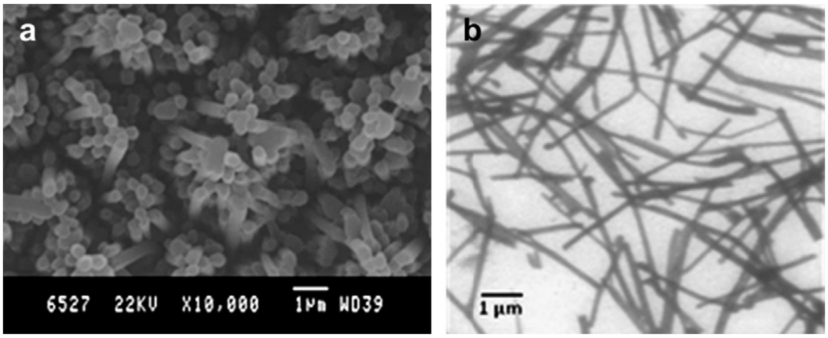

Fig. 2. a) SEM micrographs of fibers of PVAc-*b*-PAN 80/20 after dissolution of the template and b) TEM micrographs of carbon fibers prepared by graphitization of PVAc-*b*-PAN fibers 80/20 (heating rate = 5 °C/min) in the template, followed by its dissolution.

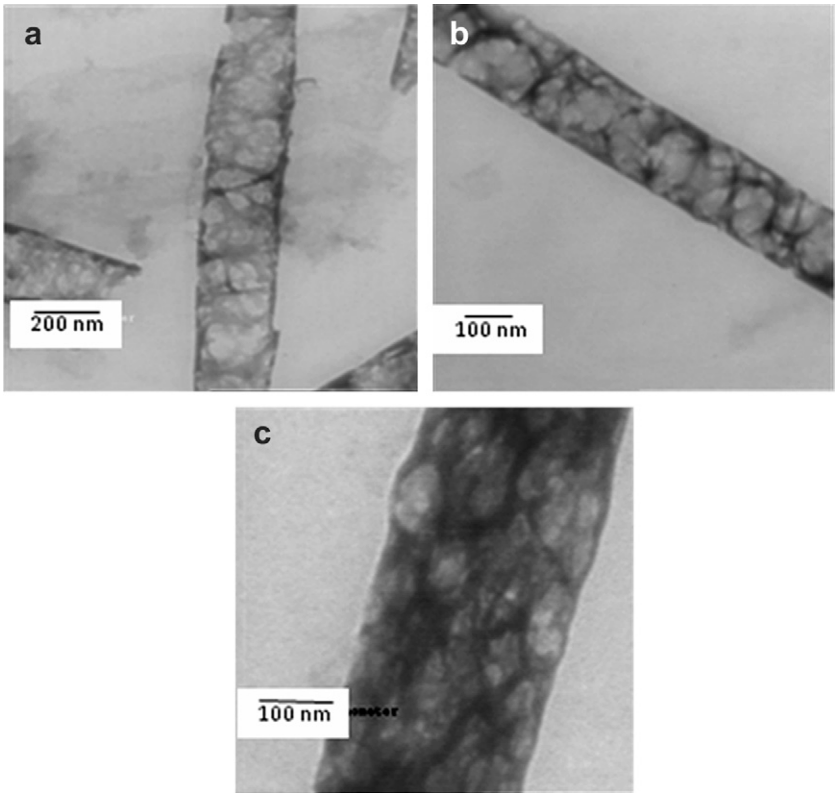

Fig. 3. TEM micrographs of carbon fibers prepared from a) PVAc-*b*-PAN 80/20, b) PVAc-*b*-PAN 55/45 and c) PVAc-*b*-PAN 36/64 at a heating rate of 20 °C/min.

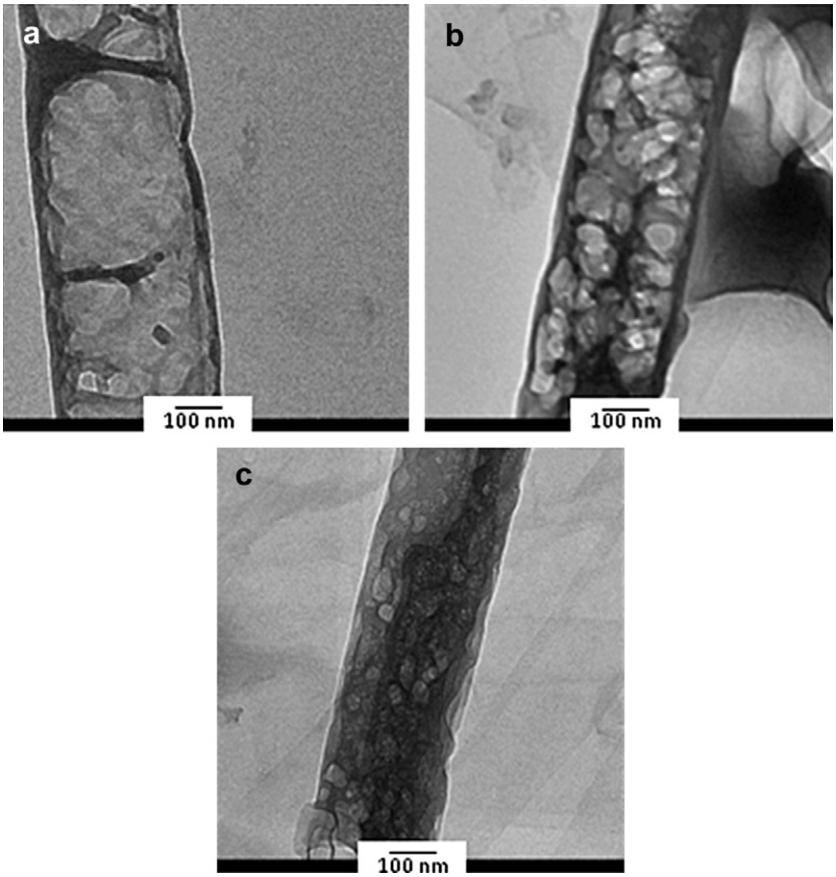

Fig. 4. TEM micrographs of carbon fibers prepared from a) PVAc-*b*-PAN 80/20, b) PVAc-*b*-PAN 55/45 and c) PVAc-*b*-PAN 36/64 at a heating rate of 5 °C/min.

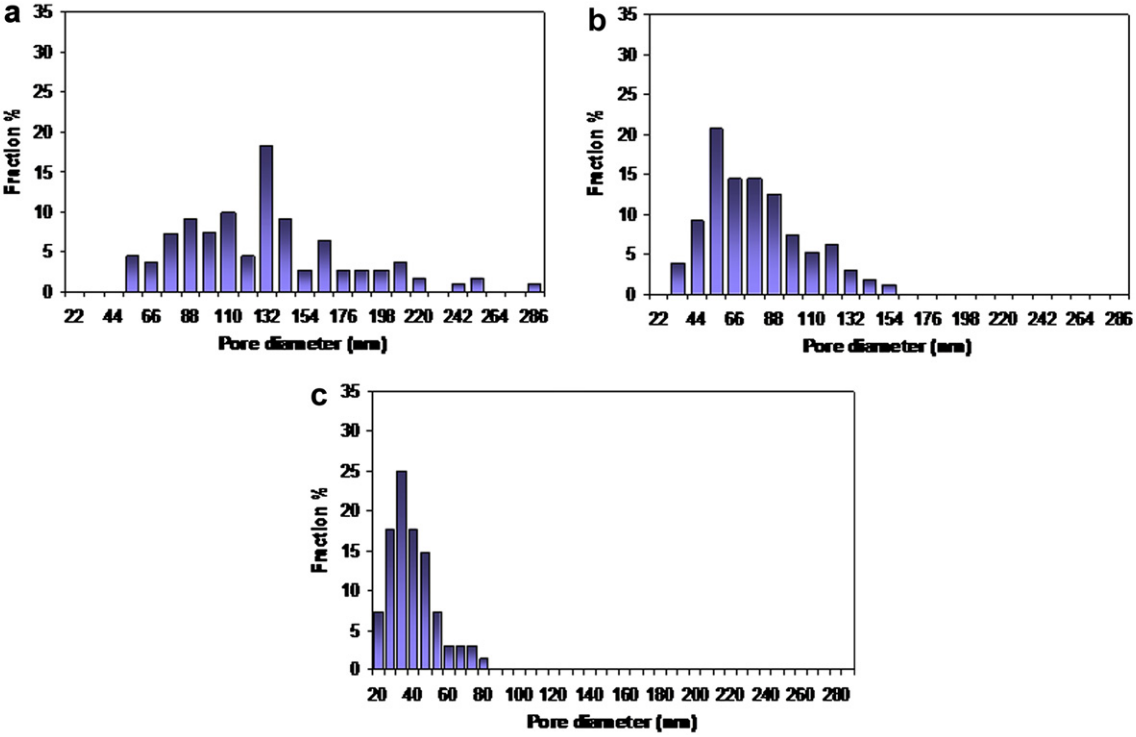

Fig. 5. Pore size distribution of carbon fibers prepared from a) PVAc-*b*-PAN 80/20, b) PVAc-*b*-PAN 55/45 and c) PVAc-*b*-PAN 36/64 at a heating rate of 5 °C/min (analysis realized on about 200 pores).

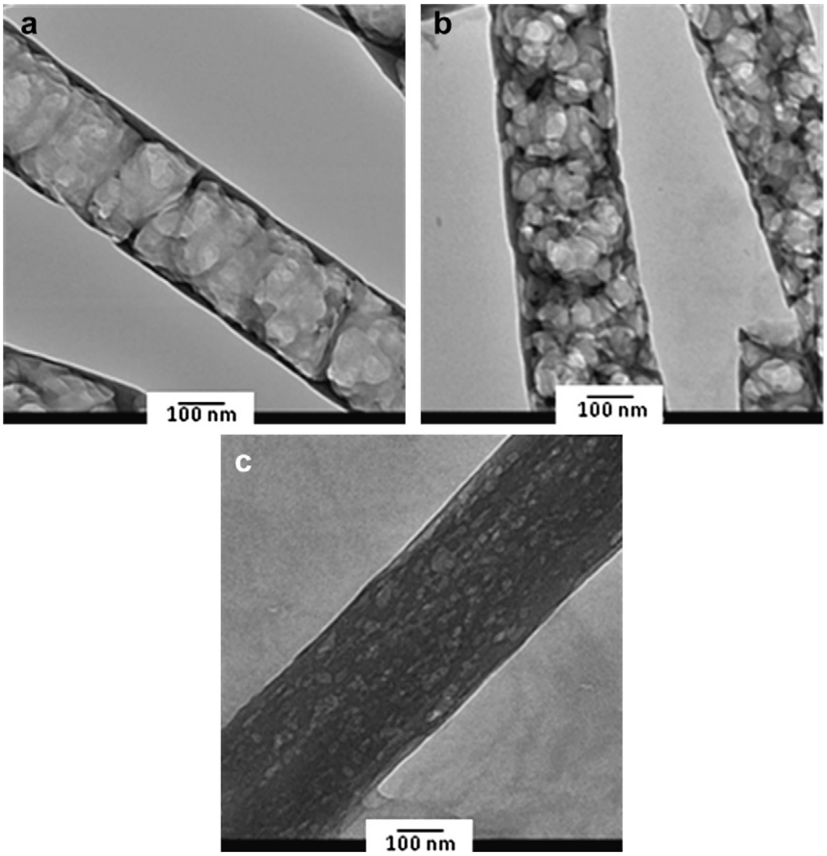

Fig. 6. TEM micrographs of carbon fibers prepared from a) PVAc-*b*-PAN 80/20, b) PVAc-*b*-PAN 55/45 and c) PVAc-*b*-PAN 36/64 at an heating rate of 1 °C/min.

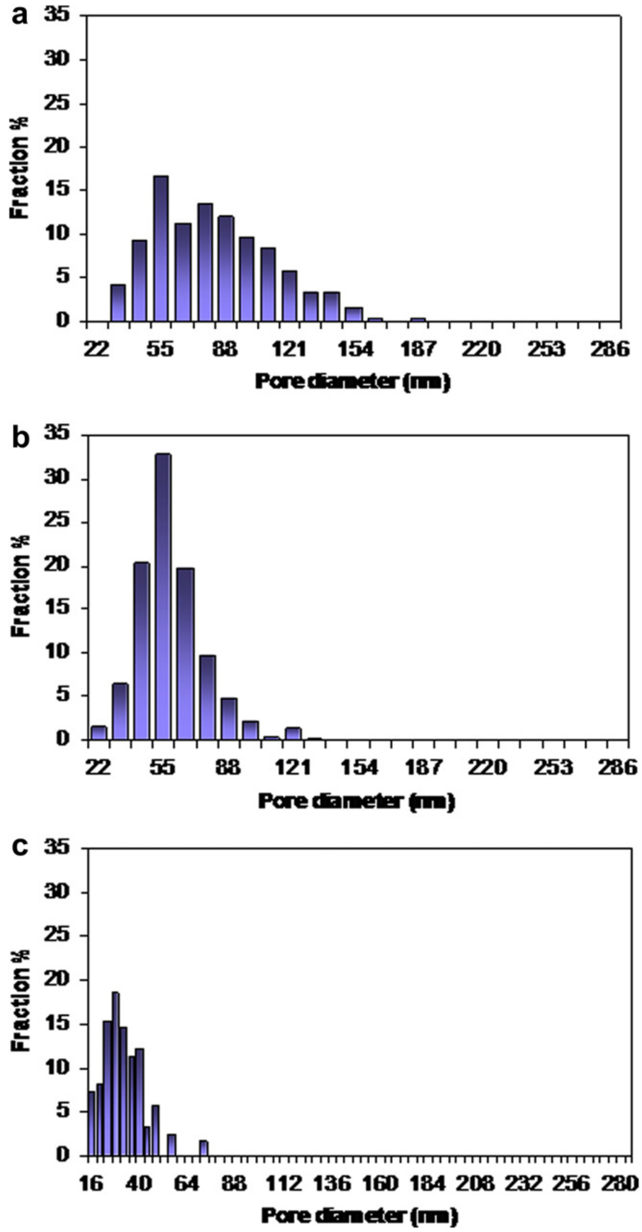

Fig. 7. Pore size distribution of carbon fibers prepared from a) PVAc-*b*-PAN 80/20, b) PVAc-*b*-PAN 55/45 and c) PVAc-*b*-PAN 36/64 at a heating rate of 1 °C/min (analysis realized on about 200 pores).

In order to promote the penetration of the copolymer in the template, a film of PVAc-*b*-PAN was deposited on the template membrane, placed between two heating plates of a compression press. A pressure of 80 bar was then applied at 180 °C during 10 min to force the migration of the copolymer in the template, thanks to the molten PVAc block that helps the copolymer to enter inside the cylindrical pores. Fig. 2 shows that this technique allows individual and completely filled fibers to be prepared.

The fibers diameter ranged from 200 to 400 nm which corresponds to the pore diameter of the AAO membranes. After dissolution of the template by a NaOH solution, the fibers tend however to collapse as a consequence of the presence of a soft PVAc block (Tg 41 °C) which renders the copolymer fibers flexible. In order to avoid any collapse of the fibers and therefore preserve their structure before the thermal treatment, the AAO membrane was only removed after the carbonization step. By this method, individualized fibers were prepared with a diameter ranging from 200 to 400 nm and with a length superior to 5 μm (Fig. 2b). In order to prove that PVAc did not degrade during the melt-compression process, a thermogravimetric analysis (TGA) under air was carried out on a PVAc homopolymer. There was no significant polymer degradation below 300 °C, suggesting that PVAc sequence of PVAc-b-PAN remained unchanged during the penetration of the copolymer in the template at 180 °C.

Three different PVAc-*b*-PAN copolymers were then used in order to study the influence of the PAN/PVAc weight ratio on the pore size of the mesoporous carbon fibers (Table 1).

Unfortunately, all our attempts to determine the morphology of the copolymer by TEM were unsuccessful since no contrasting agent (neither RuO_4 nor OsO_4) was efficient to allow distinction between the two blocks of the copolymer. However, based on several studies on the morphology of PAN-based block copolymer [19,20], we might expect that PVAc-*b*-PAN 80/20 and PVAc-*b*-PAN 36/64 block copolymers present a morphology where the low content block is dispersed inside the high content block matrix while the PVAc-*b*-PAN 55/45 should exhibit a cylindrical or co-continuous morphology.

The conversion of PAN into carbon fiber requires a two-step thermal treatment. The first step is realized at 240 °C under air to induce the cyclization of the polymer chain that renders it infusible and stabilizes the morphology for the second thermal treatment [38]. Carbonization is then realized by increasing the temperature to 600 °C under inert atmosphere. The formation of nanopores occurs during this second thermal treatment due to vaporization of the degradation product of the sacrificial block (PVAc). The heating rate during carbonization is a critical parameter because it will control the rate of gas release formed during the degradation of PVAc and the fusion of PAN cycle (release of hydrogen and other by-products [38]). Three heating rates (20, 5 and 1 °C/min) were investigated in order to determine their influence on the morphology and the pore size of the fibers. Fig. 3 shows the TEM picture of the carbon fibers prepared from the three PVAc-*b*-PAN copolymers at a heating rate of 20 °C/min. As expected, the total volume occupied by the carbon structure increased with the PAN content in the original block copolymer. For the two copolymers with low PAN content, the morphology of the resulting carbon fibers were not well defined with pores as large as the fiber diameter (Fig. 3a and b). Only PVAc-*b*-PAN 34/66 was able to produce porous fibers but pores remained quite large (>50 nm; Fig. 3c). The high diameter of the pores reveals that the carbon structure was not strong enough to resist to the high pressure generated during the gas release from the degradation product of the sacrificial block. As a consequence, the growing pores coalesced with the formation of bigger pores.

To limit this effect, lower heating rates were studied. The gas release will occur at a slower rate and, consequently, the pressure inside the pores will be lower. Fig. 4 shows that, whatever the copolymer used, the average pore diameter was greatly reduced when a heating rate of 5 °C/min is used instead of 20 °C/min. In this case, even the copolymer with low content of PAN (PVAc-*b*-PAN 80/20) is able to form porous fibers.

The distribution of the pore diameter is however quite large ranging from 50 to 250 nm with an average diameter of 130 nm. When the PAN content in the copolymer increased, the morphology of the fiber is better defined with lower pore diameter distribution (from 30 to 150 nm for PVAc-b-PAN 55/45 and from 20 nm to 80 nm for PVAc-*b*-PAN 36/64) and smaller average pore diameter (77 nm for PVAc-*b*-PAN 55/45 and 39.5 nm for PVAc-*b*-PAN 36/64) (Fig. 5).

Two effects can account for this observation. First, when the ratio PAN/PVAc in the copolymer is increased, the amount of gas generated in the fibers during the PVAc degradation is decreased consequently limiting the total fibers porosity and the pores

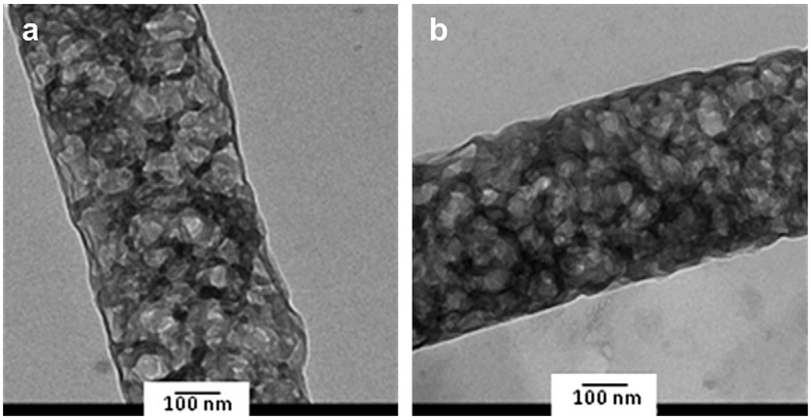

Fig. 8. TEM micrographs of carbon fibers prepared from a) PVAc-*b*-PAN 80/20 and b) PVAc-*b*-PAN 55/45 at a heating rate of 1 °C/min and in presence of $ZnCl_2$.

coalescence. Smaller pores are thus formed. Secondly, the carbon structure produced by the higher amount of PAN becomes stronger and more efficient to prevent pores coalescence.

When the heating rate is further decreased (1 °C/min), the quality of the fiber porosity is improved as depicted in Fig. 6.

Indeed, whatever the copolymer used as starting materials, the average pore diameter is decreased. The effect is particularly pronounced for the copolymer PVAc-*b*-PAN 80/20 where the average pore diameter is almost divided by two (76.8 nm vs 130.1 nm; Fig. 7). The pore diameter is however still slightly too high to consider the fibers prepared from the two low PAN content copolymers as mesoporous (pore diameter $>$ 50 nm). The pore diameter distribution is also significantly decreased. On the other hand, fibers prepared from the PAN rich copolymer (PVAc-*b*-PAN 36/64) are highly homogeneous with a pore size distribution ranging from 10 nm to 60 nm with an average pore size of 30 nm (Fig. 7). Conclusively, when starting from the same copolymer, increasing the heating rate during carbonization increases the size of the fibers pores.

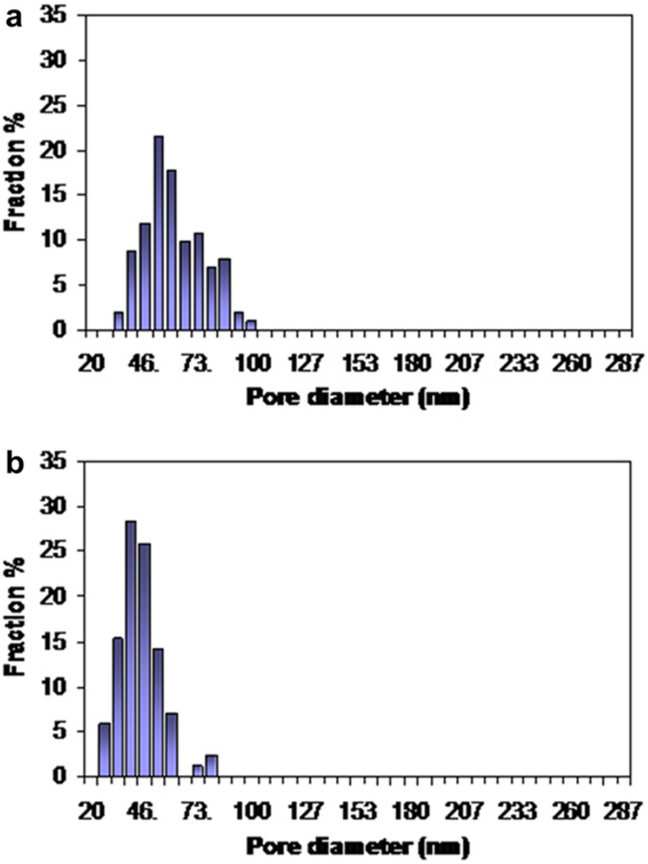

Fig. 9. Pore size distribution of carbon fibers prepared from a) PVAc-*b*-PAN 80/20 and b) PVAc-*b*-PAN 55/45 at a heating rate of 1 °C/min in the presence of $ZnCl_2$ (analysis realized on about 200 pores).

Finally, the structure of the fibers can be further improved by a more efficient stabilization of the morphology during the oxidative cyclization of the PAN chains. The resulting carbon structure would then be more resistant against the coalescence of the growing pores. Kim et al. have shown that zinc chloride can efficiently accelerate the oxidative stabilization by acting as a dehydrating agent and consequently eliminating water and inducing the aromatization of carbon [28]. 5 wt% of zinc chloride were then dispersed in PVAc-*b*-PAN block copolymer by solvent casting in DMF. After drying, carbonaceous fibers were prepared by the same method reported here above at a heating rate of 1 °C/min. Figs. 8 and 9 show that this method is efficient to decrease the pore size of the fibers allowing mesoporous materials to be prepared with the two low PAN content copolymers (pore diameter $<$ 50 nm).

These results show that with the same copolymer as starting material, a wide range of morphology can be achieved only by changing the parameters used for carbonization.

4. Conclusion

A melt template wetting method under pressure was developed to fill in nanopores of a template by a PVAc-*b*-PAN block copolymer, whose PAN block is a carbon precursor by carbonization and PVAc is a sacrificial block. Carbonization was carried out to form porous carbonaceous fibers after dissolution of the template. The composition of the copolymer and the heating rate during the carbonization steps were the main parameters investigated to tune the morphology of the porous fibers. From a same starting block copolymer, a large variety of fiber structures were prepared by modulating the heating rate during the carbonization of PAN. At high heating rate, the gas produced during the degradation of the PVAc block is quickly released resulting in fast growing pores and a large tendency to coalescence. The average pore diameter is consequently high with a large polydispersity. When decreasing the heating rate, the carbon structure is strong enough to limit the coalescence of the growing cells and mesoporous pores are obtained (diameter $\cong$ 50 nm). An increase in the PAN/PVAc relative ratio in the copolymer results expectedly to a decrease in the total porosity and an increase in the carbon structure thickness that consequently reduces more efficiently the coalescence of the growing pores.

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References

[1] Joo SH, Choi SJ, Oh I, Kwak J, Liu Z, Terasaki O, et al. Nat (London, U.K.) 2001;412:169–72.
[2] Chai GS, Yoon SB, Yu J-S, Choi J-H, Sung Y-E. J Phys Chem B 2004;108:7074–9.
[3] Siegal MP, Yelton WG, Overmyer DL, Provencio PP. Langmuir 2004;20:1194–8.
[4] Take H, Matsumoto T, Yoshino K. Synth Met 2003;135–136:731–2.
[5] Schlapbach L, Zuettel A. Nat (London, U.K.) 2001;414:353–8.
[6] Han S, Kim S, Lim H, Choi W, Park H, Yoon J, et al. Microporous Mesoporous Mater 2003;58:131–5.
[7] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. Nat (London, U.K.) 1985;318:162–3.
[8] Iijima S. Nat (London, U.K.) 1991;354:56–8.
[9] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. Sci (Washington, DC, U.S.) 2004;306:666–9.
[10] Peng M, Li D, Shen L, Chen Y, Zheng Q, Wang H. Langmuir 2006;22:9368–74.
[11] Kawashima D, Aihara T, Kobayashi Y, Kyotani T, Tomita A. Chem Mater 2000;12:3397–401.
[12] Han S, Kim M, Hyeon T. Carbon 2003;41:1525–32.
[13] Lee G-J, Pyun S-I. Carbon 2005;43:1804–8.
[14] Wang X, Bozhilov KN, Feng P. Chem Mater 2006;18:6373–81.
[15] Jia S, Tsarevsky NV, Tang C, Matyjaszewski K, Kowalewski T. Polym. Prepr. (Am Chem Soc Div Polym Chem) 2002;43:436–7.
[16] Kowalewski T. Polym Prepr (Am Chem Soc Div Polym Chem) 2002;43:46–7.
[17] Kowalewski T, Jia S. PMSE Prepr 2003;88:614.
[18] Kowalewski T, McCullough RD, Matyjaszewski K. Eur Phys J E 2003; 10:5–16.
[19] Kowalewski T, McGann JP, Yaron D, McCullough LA, Matyjaszewski K. Polym Prepr (Am Chem Soc Div Polym Chem) 2008;49:202.
[20] Kowalewski T, Tang C, Kruk M, Dufour B, Matyjaszewski K. ACS Symp Ser 2006;944:295–310.
[21] Kowalewski T, Tsarevsky NV, Matyjaszewski K. J Am Chem Soc 2002;124:10632–3.
[22] Tang C, Dufour B, Bombalski L, Matyjaszewski K, Kowalewski T. Polym Prepr (Am Chem Soc Div Polym Chem) 2005;46:497–8.
[23] Tang C, Dufour B, Kowalewski T, Matyjaszewski K. Macromolecules (Washington, DC, U.S.) 2007;40:6199–205.
[24] Tang C, Kowalewski T, Matyjaszewski K. Macromolecules 2003;36:1465–73.
[25] Tang C, Kruk M, Celer EB, Laurent A, Jaroniec M, Matyjaszewski K, et al. Prepr Symp – Am Chem Soc Div Fuel Chem 2005;50:118–20.
[26] Tang C, Qi K, Tsarevsky NV, Jia S, Dufour B, Bombalski L, et al. Polym Prepr (Am Chem Soc Div Polym Chem) 2004;45:745–6.
[27] Hulicova D, Oya A. Carbon 2003;41:1443–50.
[28] Kim C, Ngoc BTN, Yang KS, Kojima M, Kim YA, Kim YJ, et al. Adv Mater (Weinheim, Ger) 2007;19:2341–6.
[29] Zussman E, Yarin AL, Bazilevsky AV, Avrahami R, Feldman M. Adv Mater (Weinheim, Ger) 2006;18:348–53.
[30] Chen J-T, Shin K, Leiston-Belanger JM, Zhang M, Russell TP. Adv Funct Mater 2006;16:1476–80.
[31] Xiang H, Shin K, Kim T, Moon SI, McCarthy TJ, Russell TP. Macromolecules 2004;37:5660–4.
[32] Xiang H, Shin K, Kim T, Moon SI, McCarthy TJ, Russell TP. Macromolecules 2005;38:1055–6.
[33] Wang Y, Goesele U, Steinhart M. Chem Mater 2008;20:379–81.
[34] Chen J-T, Zhang M, Yang L, Collins M, Parks J, Avallone A, et al. J Polym Sci Part B Polym Phys 2007;45:2912–7.
[35] Wang Y, Qin Y, Knez M, Goesele U, Steinhart M. PMSE Prepr 2009;100:629–30.
[36] Debuigne A, Poli R, Jerome C, Jerome R, Detrembleur C. Prog Polym Sci 2009;34:211–39.
[37] Debuigne A, Warnant J, Jerome R, Voets I, de Keizer A, Cohen Stuart MA, et al. Macromolecules (Washington, DC, U.S.) 2008;41:2353–60.
[38] Xue G, Dong J, Zhang J. Macromolecules 1992;25:5855–7.