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Pore size dependent cation adsorption in a nanoporous polymer film derived from a plastic columnar phase†

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Self-supporting polymer thin films were obtained by the polymerization of an AB₃-type hydrogen-bonded complex in the plastic columnar phase. Porous polymers with pore diameters of ≈ 1.1 and ≈ 1.6 nm lined with either –COOH or –COONa groups were fabricated from the polymer thin films. Both the pore size and pore collapse influence the adsorption of cations.

Liquid crystals (LCs) have long been considered as an alternative to block copolymers for preparing nano-structured polymers by using a self-assembling bottom-up approach, especially for the preparation of nanoporous films.¹ The use of discotic LCs for the fabrication of nanoporous polymers is appealing because of their potential to introduce high-density monodisperse pores.² These dynamic viscous materials have highly desirable properties in terms of structure and morphology and are excellent candidates for being processed into polymer thin films *via* polymerisation of pendent reactive end groups in the LC periphery.^{3a}

Typically, the molecules in the LC phase are fixated using a photo-polymerisation technique, although alternative polymerisation methods are known.^{3b,c} After fixating the nano-morphology, removal of the template yields the desired monodisperse nanopores.⁴ In this manner, sub-1 nm pores have readily been obtained.^{5a} Recently, challenges such as retention of morphology after inducing porosity and aligning the pores perpendicular to the substrate have been solved; bringing this approach one step closer to implementation.^{5b} Even though many LC phases are known, in the case of discotic LCs much emphasis is given to the columnar hexagonal (Col_{hex}) phase, which yields a 1D porous polymer. Alternatively, smectic or continuous phases were used, yielding respectively 2D and 3D porous polymers,

with their own particular advantages.^{1b,5c} The major reason for using discotic LCs is their superior order compared to the latter two, yielding a high density of uniform pores.^{5d,e}

However, the use of the plastic columnar (Col_p) phase or conformationally disordered crystals⁶ instead of LCs to fabricate nanoporous films has not been demonstrated so far. The Col_p phase is characterized by 3D positional order and has significantly more long-range order than LCs. Therefore its use may potentially increase selectivity in the resultant nanoporous polymer. Such an increase is welcome for applications such as water desalination, and size-selective uptake of adsorbates. Here we describe the fabrication of an anionic nanoporous polymer from a Col_p phase that retains the nano-morphology in the porous state. However on increasing the pore size further, collapse of the bigger pores was observed. The pore size of the nanoporous polymers is found to influence the amount of dye uptake, and it is demonstrated that there is a strong decrease in the adsorption rate when the bigger collapsed pores are treated with aq. LiOH.

A gallic acid derivative, GBA, bearing an ester linkage between the gallic acid part and 4-hydroxybenzoic acid was synthesized as a viscous liquid that crystallized slowly at room temperature (see the ESI†). The hydrogen-bonded 3 : 1 complex of GBA with 1,3,5-tris(6-methyl-1H-benzotriazol-2-yl)benzene (MeTB) afforded a white solid, which transformed to a highly birefringent texture under a polarized optical microscope (POM) between 56 °C and 140 °C (Fig. 1a and Fig. S1a, ESI†). Above 140 °C, the individual components phase-separated. In agreement with the POM observation, differential scanning calorimetry (DSC) of MeTB-GBA₃ showed an endothermic transition at 55 °C (Fig. S1b, ESI†). An onset of cold crystallization at 138 °C indicated phase separation and subsequent crystallization of MeTB. Since the complex decomposed after the 1st heating run, no further transitions were observed in additional runs. The mesophase was further characterized *via* X-ray diffraction (XRD) measurements, which showed multiple peaks in the small-angle regime with a principal spacing of 3.93 nm (Fig. 2a and Table S1, ESI†). The broad peak at 0.46 nm corresponds to the mobile aliphatic chains (Fig. S2a, ESI†). However, the sharp peak at 0.35 nm represents

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Fig. 1 (a) Chemical structures and schematic representations of GBA, MeTB and MeTB-GBA₃ complex. (b) Schematic representation of a column of the plastic columnar mesophase of MeTB-GBA₃. (c) Polymerization of the complex in the plastic columnar mesophase followed by treatment with DMSO resulted in the formation of [S]-COOH. (d) [S]-COOH afforded [S]-COONa by reacting with aq. NaOH solution. (e) A [B]-COONa porous film was obtained from the polymer film by the hydrolysis of the ester linkage. (f) Schematic illustration of efficient adsorption of MB in the pores of [B]-COONa. (g) [B]-COONa afforded [B]-COOH after acidic treatment. Schematic illustrations of the presence of collapsed and open pores in H₂O and THF/H₂O (1 : 1 v/v) of [B]-COOH and their propensity of reactions with LiOH in aq. solution.

the interdisc distance ($d_{(001)}$) of the columnar phase (Fig. S2a, ESI†). The presence of multiple Bragg peaks in the low-angle regime and shearability of the complex in the mesophase region indicate an ordered Col_p phase (Fig. 1b).⁶

The 3 : 1 complex between GBA and the non-methylated template, TB, had a similar texture in POM (Fig. S3a, ESI†). In DSC, the crystalline to Col_p phase transition increased from 55 °C to 70 °C for TB-GBA₃ (Fig. S3b, ESI†). The mesophase of TB-GBA₃ showed a similar reflection pattern as MeTB-GBA₃, indicating a Col_p phase (Fig. 2a and Fig. S2a, ESI†). The formation of a Col_p phase in the present case is distinctly different from the Col_{hex} LC phases observed for similar complexes of TB/MeTB that were reported previously.^{2c,5b}

A mixture of MeTB-GBA₃ or TB-GBA₃ (10 mg in 0.3 mL 4 : 1 CHCl₃/MeOH (v/v)) and Grubbs' 2nd gen. catalyst (0.2 mg in 30 μL CHCl₃) were dried under vacuum while making a thin film on a glass surface *via* rotational molding and then placed in a vacuum oven at 100 °C for 12 h. The increased order of the Col_p phase did not hamper the acyclic diene metathesis (ADMET) polymerization to take place, crosslinking the peripheral double

Fig. 2 (a) XRD data of the mesophases formed by TB-GBA₃ and MeTB-GBA₃ complexes at 100 °C. (b) Comparison of principal spacing of the monomer complexes, polymers and different porous polymers. (c) A picture of a self-supporting polymer thin film obtained after polymerization of the MeTB-GBA₃ complex. (d) POM image of the polymer film, scale denotes 10 μm. (e) FT-IR spectra of the MeTB-GBA₃ complex before and after polymerization. (f) Comparison of FT-IR spectra of the native polymer and the porous polymer, [S]-COOH.

bonds of the complexes resulting in the formation of self-supporting native polymer films (Fig. 2c). The high conversion of the monomer was confirmed by the disappearance of the =C–H bending vibration bands at 908 and 992 cm^{−1} (Fig. 2e). In addition, the intensity of the C=C stretching vibration at 1639 cm^{−1} of the double bonds also diminished significantly after polymerization, indicating a high degree of conversion. The insolubility of the polymer film in the organic solvents CHCl₃, MeOH, EtOH, DMF and DMSO also showed that the material was crosslinked. Additionally, the polymer film remained birefringent under POM, indicating retention of the nano-morphology of the Col_p phase (Fig. 2d). XRD measurements of the polymer films confirmed the retention of the nanostructure. A decrease of the principal spacing from 3.93 to 3.91 nm for MeTB-GBA₃ and 3.98 to 3.73 nm for TB-GBA₃ was observed (Fig. 2b and Table S1, ESI†).

The polymer film derived from MeTB-GBA₃ was immersed in DMSO and shaken for 2 days, resulting in complete removal of the MeTB template as confirmed by UV/Vis spectroscopic studies of the extracted solution (Fig. S4, ESI†). Template removal furnished porous polymer thin films with ≈1.1 nm pores lined with –COOH groups on the pore surface (Table S2, ESI†). The films with ≈1.1 nm pores are further designated as [Small-pore]-COOH or [S]-COOH (Fig. 1c). The disappearance of the N–H stretching vibration at 3300 cm^{−1} and emergence of the –C=O vibration at 1693 (asymmetric stretch) and 1586 cm^{−1}

(symmetric stretch) further confirmed the removal of MeTB and formation of free -COOH groups on the pore surface (Fig. 2f).^{2c,4a}

The -COOH groups at the pore surface of [S]-COOH (film thickness $\approx 15\ \mu\text{m}$) were reacted with an excess of 10 mM aq. NaOH solution for ≈ 10 minutes to furnish polymer films lined with -COONa groups, [S]-COONa (Fig. 1d and Fig. S8a, ESI†). FT-IR spectroscopy showed that the asymmetric and symmetric stretching vibrations of the carbonyl groups shifted from 1693 to 1556 cm^{-1} and 1586 to 1396 cm^{-1} respectively upon treating with aq. NaOH solution, in line with the quantitative conversion of [S]-COOH to [S]-COONa (Fig. 3a).^{4a} However, during the aq. NaOH treatment, the vibration band at 1732 cm^{-1} , corresponding to the -C=O stretching of the ester linkage, remained unchanged indicating that the inner ester linkage did not hydrolyze under these basic conditions (Fig. 3a). The porous polymer films, [S]-COOH and [S]-COONa, were further characterized by XRD. The principal spacing slightly decreased from 3.91 to 3.74 nm (polymer to [S]-COOH) and from 3.91 to 3.75 nm (polymer to [S]-COONa) indicating that the pores remained almost intact and did not collapse after template removal (Fig. 2b, Fig. S2b and Table S1, ESI†).

The ester linkage within the GBA part of the polymer was hydrolyzed with 1 M NaOH at 46 °C for 12 h, resulting in the removal of MeTB and the benzoic acid moiety of GBA from polymerized MeTB-GBA₃, accounting for ≈ 31 wt% of the material. This resulted in the formation of a porous anionic polymer ([Big-pore]-COONa or [B]-COONa) with a larger pore diameter of ≈ 1.6 nm (Fig. 1e and Table S2, ESI†). Indeed, a native polymer film (6.00 mg) afforded 4.18 mg of the [B]-COONa film, confirming almost quantitative removal of the MeTB and the benzoic acid moiety from the native polymer. Solid state ^{13}C NMR studies further confirmed the formation of the [B]-COONa film

(Fig. S5, ESI†). Hydrolysis of the ester linkage was evidenced from the disappearance of the 1732 cm^{-1} peak in the resultant porous polymer (Fig. 3b). In addition, two new peaks at 1556 and 1375 cm^{-1} emerged after hydrolysis and were assigned to the asymmetric and symmetric vibrations of the -C=O stretch of -COONa moieties on the pore surface.^{4a}

Porous polymer [B]-COONa was converted to [B]-COOH by treating the film with ethanolic HCl solution (Fig. 1g), resulting in a shift of the asymmetric and symmetric stretching vibration bands to 1685 and 1585 cm^{-1} , indicating the presence of -COOH moieties on the pore surface (Fig. S6, ESI†). XRD data showed that the principal spacing had decreased significantly from 3.91 nm in the polymer to 2.95 nm in [B]-COOH and 2.87 nm in [B]-COONa (Table S1, ESI†), indicating that the pores in [B]-COONa and [B]-COOH are collapsed probably due to the large pore size.

The anionic pores in [S]-COONa and [B]-COONa are expected to selectively adsorb cationic species.^{1b} The adsorption of cationic and anionic dyes was tested by treating the anionic films with aq. dye solutions. Both the films of [S]-COONa and [B]-COONa did not adsorb anionic sodium fluorescein (SF) from solution, even when kept immersed for several hours (Fig. S7, ESI†). [S]-COONa films (thickness $\approx 15\ \mu\text{m}$, 0.24 mg) adsorbed a small amount of cationic methylene blue (MB) from solution over the course of 20 h. (Fig. 3c and Fig. S8a, S9a, ESI†). However, [B]-COONa films (thickness $\approx 14\ \mu\text{m}$, 0.2 mg) bearing large pores rapidly adsorbed MB from a mixed solution of MB (6.4 μM) and SF (6 μM), even though the pores are collapsed in the dry polymer (Fig. 1f, 3d and Fig. S8b, ESI†). The green solution turned orange, corresponding to the color of SF and the porous polymer film became dark blue after adsorption from the mixture (Fig. S9b, ESI†). It is important to mention that the size of the bigger pores (≈ 1.6 nm) is larger than the size of the MB dye, ≈ 0.6 nm along the short axis (Fig. S11, ESI†).^{5b} Further analysis showed that after 20 h, [B]-COONa adsorbed 4.5 times more MB than [S]-COONa although the initial rate of adsorption is almost the same (Fig. S8c, ESI†). When we took two cationic dyes MB and Rhodamine 6G (R6G, ≈ 0.8 nm along the short axis) of different sizes, the porous film of [B]-COONa showed simultaneous adsorption of both dyes (Fig. S10a and S11, ESI†). In direct competition between R6G and an even bigger dye molecule, Alcian blue 8GX (AB8G, ≈ 1.4 nm along the short axis), AB8G was adsorbed faster in the pores of [B]-COONa, probably because of its higher positive charge, while adsorption of the smaller R6G dye was slowed down due to the presence of AB8G (Fig. S10c, ESI†).

Ion adsorption in [B]-COOH and [S]-COOH was fast and quantitative with 10 mM aq. NaOH, KOH and CsOH solutions (Fig. S12a and b, ESI†). In contrast, LiOH was adsorbed more slowly in the porous polymer films of [S]-COOH or [B]-COOH than the other alkali metal hydroxides. Complete conversion of [S]-COOH by 10 mM aq. LiOH solution took approximately 1 h. FT-IR analysis showed that the -C=O stretching vibration of the -COOH groups at 1693 cm^{-1} gradually reduced in exchange for a new vibration band at 1556 cm^{-1} , which was assigned to the asymmetric stretching vibration of carboxylate groups (Fig. 4a). Surprisingly, [B]-COOH adsorbed Li^+ ions even more slowly from solution. FT-IR analysis showed that the formation of [B]-COOLi was not complete even after 12 h (Fig. 4b). The slower

Fig. 3 (a) Comparison of FT-IR spectra of the porous polymers [S]-COOH and [S]-COONa. (b) Comparison of FT-IR spectra of the native polymer with the porous polymer, [B]-COONa. (c) Time dependent adsorption of MB (6.4 μM) by the [S]-COONa porous film. (d) Monitoring adsorption of the cationic MB (6.4 μM) in the presence of anionic SF (6 μM) by an anionic [B]-COONa porous film in an aq. medium using UV/Vis absorption spectroscopy.

Fig. 4 (a and b) Monitoring the reaction of [S]-COOH and [B]-COOH with 10 mM aq. LiOH solution at different time intervals using FT-IR spectroscopy.

adsorption of Li^+ ions in the case of [B]-COOH might be a consequence of the pores staying in the collapsed state during conversion to the salt (Fig. 1g). The larger size of hydrated Li^+ ions compared to the other hydrated alkali metal ions likely causes the slower diffusion of Li^+ ions in the pores.^{2c} However, in the case of [S]-COOH, the pores remained open before and after the reaction with aq. LiOH solution, allowing a faster uptake of Li^+ when compared to [B]-COOH.

The assumption that the collapsed state of the pores in [B]-COOH hinders the passage of Li^+ was further confirmed by an experiment, in which porous polymer [B]-COOH adsorbed Li^+ ions quantitatively within 15 min, if the reaction was performed in THF:H₂O (1:1 v/v) instead of water (Fig. S13, ESI†). In the mixed solvent, the film swelled visibly, opening the collapsed pores and allowing much faster uptake of Li^+ ions. (Fig. 1g).

In conclusion, nanoporous polymers have been prepared from a Col_p phase. By judicious choice of chemical treatment, porous polymer thin films with ≈ 1.1 nm diameter small pores or ≈ 1.6 nm diameter bigger pores were produced. Anionic porous polymers bearing -COONa groups have been prepared previously from LC derived polymers;^{4a,5a} however, the pore size of these polymers was not tunable. [S]-COONa and [B]-COONa bearing -COONa groups in the pore surface selectively adsorbed a cationic dye in preference over an anionic dye, with 4.5 times more dye adsorbed in the big pores of [B]-COONa after 20 h. Unlike dye adsorption, the uptake of Li^+ ions by the large collapsed pores of [B]-COOH was much slower than that by the small open pores of [S]-COOH. The current work highlights different factors that determine the adsorption of dyes in [B]-COONa and [S]-COONa, and binding of alkali metal ions

in [B]-COOH and [S]-COOH. Fabrication of porous polymer films by using the Col_p phase demonstrated the applicability and the versatility of the present approach, perhaps bridging the gap between LC-based porous polymers and aluminosilicate, zeolite type porous solids.

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Conflicts of interest

There are no conflicts to declare.

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