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Influence of branching of polythiophenes on the microporosity

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We report a chain growth polymerization of a branched polythiophene (BT) using a Pd(Ruphos) catalyst, as a promising route to synthesize microporous conjugated polymers (CPs) with well-defined structures. From N₂ adsorptions/desorption isotherm measurements, a Brunauer-Emmett-Teller (BET) surface area of 40.7 m² g⁻¹ is calculated for the BT, significantly higher than that of the linear poly(3-hexylthiophene) (P3HT) (25.7 m² g⁻¹). The same trend is confirmed by simulations of the two polymer structures, from which a geometric surface area (SA_{geo}) of 140±15.8 m² g⁻¹ is calculated for the BT, much more higher than for the P3HT with a SA_{geo} of 6.7±7.1 m² g⁻¹. Moreover, the BT is soluble in common organic solvent and is readily processed in membrane with a CO₂/N₂ selectivity up to 24.

1. Introduction

Conjugated microporous polymers (CMPs) have found increasing interest as potential materials for gas storage and separation.¹⁻⁶ The combined chemical and thermal stability of conjugated polymers (CPs) allow to potentially consider these organic materials to be complementary to their inorganic counterparts such as zeolites, ceramic and carbon molecular sieves.⁷ To obtain a microporous structure, CPs are either crosslinked to form a network of covalently interconnected chains,⁴ or a (hyper)branched structure is formed to disrupt the π -stacking of polymer backbones.² The former procedure “crosslinking” however often results in insoluble polymer network difficult to process in membranes, and therefore the branching technique is more appealing.^{2,7} Among the investigated branched CPs, polythiophene (PT), the benchmark CP and the most investigated in electro-optical applications, has scarcely been reported.^{1,3,4} The reason for this can be ascribed to a lesser developed controlled polymerization of branched PTs in contrast to their linear counterparts.⁸⁻¹⁰ This explains why almost all investigated branched PTs in gas separation and/or gas storage were synthesized via a non-controlled route, mostly by chemical oxidative polymerization.^{3,4,11,12} The latter has several drawbacks. First, during chemical oxidative polymerization crosslinking can still happen leading in the formation of insoluble polymers impossible to process in membranes;^{7,13,14} second, a stoichiometric amount of catalyst used, e.g. FeCl_3 , which can be difficult to separate from the final product,^{4,11,12} and third, the structure of polymers obtained in this manner is poorly defined with inferior physical properties.^{15,16} To overcome the above disadvantages of a chemical oxidative polymerization, in this manuscript we aimed on designing a new thiophene monomer scaffold, which can be polymerized via a controlled chain-growth polymerization, to yield a well-defined branched PT with higher microporosity than linear PTs for potential applications in gas storage and/or separation. The microporosity of the polymers can be revealed by measuring N_2 adsorption isotherms and BET surface areas. The latter is widely used to probe the material microporosity.^{1,3,4}

In addition, simulations were carried out on the branched PT and the linear P3HT to study the structural influence on the polymer microporosity.

2. Experimental

2.1. Syntheses

2.1.1. Monomer

*3,4-Dimethylthiophene (2)*¹⁷

3,4-Dibromothiophene (15.0 g, 62.0 mmol) and 1,3-bis(diphenylphosphino)propane nickel chloride [Ni(dppp)Cl₂] (0.835 g, 1.55 mmol) were dissolved in dry diethylether (Et₂O) (200 mL) and cooled to 0 °C. To this, a solution of methylmagnesiumbromide (MeMgBr, 3M in Et₂O) (52.0 ml, 155 mmol) was added dropwise under argon atmosphere. After the addition, the reaction mixture was refluxed for 3 h and stirred overnight at room temperature (rt). The reaction mixture was poured in a HCl-solution (200 mL, 2M) and the organic layer was separated. The latter was washed with brine, dried over MgSO₄ and filtered. The solvent was evaporated in vacuo to obtain a colorless oil (6.38 g, 92 %).

¹H NMR (300 MHz, CDCl₃, Me₄Si, δ): 6.88 (s, 2H), 2.16 (s, 6H)

2-Bromo-3,4-dimethylthiophene (3)

N-bromosuccinimide (NBS) (10.0 g, 56.6 mmol) was added portion wise to a stirred solution of 3,4-dimethylthiophene (6.34 g, 56.6 mmol) in THF (250 mL) cooled at 0 °C. After the addition, the reaction mixture was allowed to warm to rt and it was stirred overnight. The reaction mixture was poured into a saturated solution of NaHSO₃ (200 mL) and THF was evaporated in vacuo. The remainder aqueous solution was extracted with heptane. The organic fraction was subsequently washed with a NaOH-solution (2M), a solution of NaHCO₃ (20 %), brine and dried over MgSO₄. The solvent was removed in vacuo and the mixture was purified by column

chromatography (silicagel, heptane). The product was isolated as a light yellow oil (5.81 g, 54 %).

^1H NMR (300 MHz, CDCl_3 , Me_4Si , δ): 6.85 (s, 1H), 2.17 (s, 3H), 2.09 (s, 3H)

*3,4-Dimethyl-2-(3-thienyl)thiophene (4)*¹⁸

3-Thienylboronic acid (4.75 g, 37.0 mmol), $\text{Pd}(\text{OAc})_2$ (0.141 g, 0.610 mmol), $\text{P}(t\text{Bu})_3\cdot\text{HBF}_4$ (0.214 g, 0.730 mmol) were added to 250 ml flask and flushed with Ar. To this, a solution of compound **3** (5.81 g, 30.3 mmol) in *n*-butanol (150 mL) was cannulated, and the mixture was stirred for 15 min. Next, an alkaline solution of NaOH (2.08 g, 52.0 mmol) in degassed deionized water (50 mL) was cannulated to initiate the reaction which was stirred for 2h. The organic layer was separated and the aqueous layer was extracted with Et_2O (3x50 mL). The combined organic extracts were concentrated and the residue was purified by flash column chromatography (silicagel, heptane) to yield a colorless oil (5.01 g, 87 %).

^1H NMR (300 MHz, CDCl_3 , Me_4Si , δ): 7.38-7.34 (m, 1H), 7.30-7.27 (m, 1H), 7.24-7.20 (m, 1H), 6.84 (s, 1H), 2.22 (s, 3H), 2.19 (s, 3H)

MS: $\text{M}^+(\text{m/z})=194.01$

2-Bromo-3,4-dimethyl-5-[3-(2-bromo)thienyl]thiophene (5)

Following the same procedure as for the preparation of compound **3**, NBS (9.06 g, 51.0 mmol) and compound **4** (4.98 g, 25.5 mmol) were used. The mixture was purified by recrystallization in heptane to obtain a solid (4.45 g, 51 %).

^1H NMR (300 MHz, CDCl_3 , Me_4Si , δ): 7.29 (d, $J = 5.72$ Hz, 1H), 6.89 (d, $J = 5.72$ Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3 , Me_4Si , δ): 137.5, 136.0, 134.7, 130.0, 125.7, 112.7, 109.1, 14.7

Mp: 64-65 °C, MS: $\text{M}^+(\text{m/z})=351.98$

2-Bromo-5-iodo-3-[2-(3,4-dimethyl-5-bromo)thienyl]thiophene (6)

To a solution of compound **5** (4.37 g, 12.2 mmol) in DCM (70 mL) were added iodine I₂ (1.54 g, 6.10 mmol) and PhI(OAc)₂ (1.96 g, 6.10 mmol). The reaction mixture was allowed to react to full conversion. At completion, the mixture was poured to a saturated solution of NaHSO₃ (150 mL) and the organic layer was separated, washed with brine and dried over MgSO₄. The solvent was evaporated and the phenyl iodide was removed via a vacuum distillation to give a solid (4.67 g, 80 %).

¹H NMR (300 MHz, CDCl₃, Me₄Si, δ): 7.05 (s, 1H), 2.13 (s, 3H), 2.06 (s, 3H); ¹³C NMR (400 MHz, CDCl₃, Me₄Si, δ): 139.2, 137.5, 136.6, 128.50, 115.3, 109.5, 72.0, 14.5

Mp: 69-70 °C, MS: M⁺(m/z)=477.5

2.1.2. The hyperbranched polythiophene (**BT**)

The BT was prepared as follows: to a solution of compound **6** (1.40 g, 2.92 mmol) in THF (15 mL) was added a solution of isopropylmagnesium chloride lithium chloride (*i*PrMgCl.LiCl, 1.25 M in THF) (2.33 mL, 2.92 mmol,) under Ar atmosphere to form the corresponding Grignard compound after a reaction time of 45 min. A sample aliquot was withdrawn, quenched in D₂O, extracted with Et₂O and concentrated to verify the conversion with ¹H NMR. Next, the formed Grignard compound was cannulated to an Ar purged flask containing dry ZnBr₂ (1.35 g, 6.00 mmol) and stirred for 45 min to form the organozinc monomer. To this, the Pd(Ruphos) catalyst (60.0 mg, 0.070 mmol), dissolved in dry THF (2 mL), was added to initiate the polymerization. After a polymerization time of 3 h, an acidified THF-solution was added to quench the reaction. The polymerization mixture was precipitated in methanol and filtered off. The precipitate was Soxhlet extracted subsequently with methanol, acetone and chloroform. The chloroform fraction was concentrated, added to methanol to precipitate the polymer. The polymer was filtered off and dried in vacuum to give the crude polymer (0.410 g, 72 %).

2.1.3. The poly(3-hexylthiophene) (P3HT)¹⁷

To a solution of 2-bromo-5-iodo-3-hexylthiophene (5.03 g, 13.5 mmol) in dry THF (100 mL) was added a solution of isopropylmagnesium chloride lithium chloride (*i*PrMgCl.LiCl, 1.25 M in THF) (10.7 ml, 13.5 mmol,) under Ar atmosphere and stirred at rt. After 45 min reaction time a sample aliquot was withdrawn, quenched in D₂O, extracted with Et₂O and concentrated to verify the Grignard conversion with ¹H NMR. Next, the formed Grignard compound was cannulated to an Ar purged flask containing a Ni(dppp)Cl₂ catalyst (48.8 mg, 0.090 mmol) to initiate the polymerization. After a polymerization time of 3 h, an acidified THF-solution was added to stop the reaction. The polymerization mixture was precipitated in methanol and filtered off. The precipitate was Soxhlet extracted subsequently with methanol, acetone and chloroform. The chloroform fraction was concentrated, added to methanol to precipitate the polymer. The polymer was filtered off and dried in vacuum to give the polymer (2.010 g, 93 %).

2.2. Membrane fabrication

A polymer solution (5 wt% in CHCl₃) was spin coated on top of a porous polyimide (PI) support. The coated polymer was sealed with a highly porous polydimethylsiloxane (PDMS) layer and the obtained thin film composite (TFC) membrane was dried in an oven at 140 °C for 1 h. The support was prepared by a deposition of a PI solution (Matrimid 22 wt%, N-methyl-2-pyrrolidone (NMP) 48.75 wt % and THF 29.25 wt %) onto a NMP saturated non-woven PP/PE fabric (Novatex) by means of an automated casting knife (Braive Instruments, Belgium) set at 250 or 200 μm and 1.2 m.min⁻¹. After casting, the solvent was let evaporated for a short time (1-2 min) and the membrane was immersed for 1 h in a deionized water bath for coagulation. To crosslink the support, it was immersed for 1 h in a methanol solution containing 5 wt% of hexamethylenediamine, rinsed with methanol and stored in the same solvent ready for use.^{19,20}

The sealing solution, however, was prepared by dissolving the PDMS (RTV 615 – two component Kit, Momentive Performance Materials) in hexane (20 wt% total, 9:1 A-B ratio) and heated at 60 °C for 1 h to initiate the crosslinking.²¹

2.3. Characterizations

2.3.1. Monomer and polymers

¹H-NMR and ¹³C-NMR spectra of the synthesized molecules were recorded using Bruker Avance NMR (300 and/ or 400 MHz) to reveal their structures. The samples were dissolved in CDCl₃ with tetramethylsilane (Me₄Si) as internal standard. To determine the polymer molar mass and dispersity, a Shimadzu 10 AVP GPC device was employed. About 2 mg of polymer was dissolved in 2 ml of THF and the solution was filtered through micropores (0.20 µm diameter) before injecting in the device. The GPC was calibrated with polystyrene (PS) standards using THF as eluent.

2.3.2. Microporosity and gas separation

The crude polymer was subjected to nitrogen adsorption/desorption isotherms at 77 K to measure the BET surface area. To analyze the gas separation performance, the polymer was casted in thin film composite (TFC) membrane. The gas separation experiment was performed using a high-throughput gas separation (HTGS) which functioning is described elsewhere.²² The membrane cell temperature was adjusted at 26 °C, the feed pressure at 3 bar and the permeate side was kept at vacuum. The permeate gas composition was determined by a compact gas chromatograph (cGC, Interscience), and the permeability through the membrane was calculated by monitoring the gas pressure in the cylinder using equation 1.

$$P_i = \frac{273 \cdot 10^6}{760} \frac{y_i V}{AT \left(\frac{76}{14.7} \right) x_i P_2} \frac{dP}{dt} \quad (1)$$

From the above equation 1, x_i and y_i represent the mole fractions of i gas in the upstream and

downstream respectively. V is the downstream volume in cm^3 and dp/dt is the increase pressure rate. While A refers to the membrane area in cm^2 , T is the cell temperature in kelvin and P_2 is the feed pressure in Psi. The single gas selectivity α_{ij} between gas component i and j was determined by a ratio of their respective permeabilities ($\alpha_{ij} = \frac{P_i}{P_j}$). However, the mixed gas selectivity was obtained by taking the mole fractions on downstream (y_i, y_j) and upstream (x_i, x_j) of the two gases as shown in equation 2.

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \quad (2)$$

2.4. Simulations

To simulate the macromolecular structure influence on the microporosity, united atom (UA) model, GAFF (general amber force field)²³ and TraPPE (transferable potentials for phase equilibria force field)²⁴ were used as the sources for bonded and non-bonded interaction parameters, respectively. A in-house code called lammmpsBuilder was used to generate the initial simulation box, input files including monomeric topology, new connections between monomers and coordinates needed to be predefined. 10 identical polymer chains were inserted into the simulation box, the degree of polymerization for single chain was set to 15. A 21-step compression procedure was utilized to equilibrate the membrane samples and to bring the samples to realistic densities.²⁵ Porosity characteristics like geometric surface area (SA_{geo}), pore volume (V_{pore}), fractional free volume (f) and the geometric pore size distribution (PSD) were calculated by poreBlazer,^{26,27} it should be mentioned here that f cannot be calculated by poreBlazer directly, but f has the relationship to void volume (ψ) which can be obtained from poreBlazer, as shown in equation 3.

$$f = \frac{V_{vdw} - 1.3(V_{vdw} - \psi)}{V_{vdw}} \quad (3)$$

Grand Canonical Monte Carlo Simulation (GCMC) method was used to measure the adsorption

behaviors including adsorption isotherms and solubility of **both polymer membranes**. All calculations **were performed** using Monte Carlo for complex chemical systems (MCCCS) Towhee software 7.2.0.²⁸ Chemical potentials for four types of gases (CO₂, CH₄, O₂ and N₂) **were calculated** in the isobaric isothermal (NPT) ensemble using Widom insertion method.²⁹ For single GCMC simulation, the first half of 3 million steps was used for equilibrium and the second half **was averaged** to obtain the results.

During the simulation, polymer matrix **was treated** as fixed and rigid. The total adsorption (η_{tot}) obtained from Towhee **was converted** to excess adsorption (η_{exc}) by equation 4.

$$\eta_{exc} = \eta_{tot} - \rho_g V_{pore} \quad (4)$$

Where ρ_g is the gas density **which was taken** from NIST Webbook.³⁰ The solubility coefficient is defined as the pressure normalized concentration of sorbent present within the polymer at equilibrium, as shown in equation 5.

$$S = \frac{c(p)}{p} \quad (5)$$

The diffusivity has the relationship direct to fractional free volume (f), considering simplicity, it can be calculated by using equation 6, where α_D and β_D are empirical parameters and can be found in table 3 in the literature.³¹

$$D = \alpha_D \cdot \exp(\beta_D \cdot f) \quad (6)$$

All properties mentioned above **were averaged** of five parallel samples **for each polymer**.

3. Results and Discussions

3.1. Syntheses

3.1.1. Monomer

The precursor monomer **6** was synthesized as depicted in Scheme 1. From 3,4-dibromothiophene, methyl groups were introduced at positions 3 and 4 via a Kumada coupling reaction using a methylmagnesiumbromide solution and Ni(dppp)Cl₂ as catalyst. The alkyl side chain

was used to improve the solubility of the resulting polymer, and more interestingly it was kept as short as possible so that it cannot fill up the formed micropores. The double methylated thiophene was brominated at position 2 and coupled with 3-thienylboronic acid via a Suzuki reaction to form a 3,2'-bithiophene derivative. The latter compound was double brominated (positions 2 and 5') and iodinated at position 5 to give the precursor monomer **6**. The two C-Br bonds constituted the active sites by which the catalyst can oxidatively insert and the propagation can both occur to give a hyperbranched structure.³² The C-I bond, however, enabled a selective metalation of the precursor monomer prior the in situ formation of the corresponding 5-organozinc monomer (step *vi* in Scheme 2).^{17,33} The latter can therefore be polymerized via chain growth using a Pd(Ruphos) catalyst to give a well-defined hyperbranched PT.⁹

Scheme 1

3.1.2. Polymerization of the hyperbranched polythiophene (BT)

The branched polymer (BT) was synthesized from a reaction between the in situ generated organozinc monomer **8** and the Pd(Ruphos) catalyst as depicted in Scheme 2. The monomer was of AB₂ type where A (C-ZnBr) deactivates B (C-Br) to prevent a reaction between the monomers. The A function on the monomers can only react with the active B on either the catalyst or on the propagating polymer chain as illustrated in Scheme 2.³² To obtain a higher degree of branching, it was decided to use the Pd(Ruphos) catalyst. In contrast to e.g. Ni catalysts, the Pd(Ruphos) can get loose from one growing chain and oxidatively insert in an active C-Br bond of another chain in the polymerization mixture. This behavior enables to achieve a higher degree of branching with the Pd(Ruphos) catalyst as it was reported by Steverlynck *et al.*⁹

Scheme 2

3.2. Characterizations

3.2.1. Monomer and polymers

The structures of the synthesized molecules were confirmed by an analysis of their ^1H NMR and/or ^{13}C NMR spectra as can be seen in the supporting information (SI). The BT had a weight average molar mass of $4.5 \text{ kg}\cdot\text{mol}^{-1}$ and a dispersity of 1.85 as recorded by GPC towards polystyrene standards. However, this was still a relatively low molar mass for fabricating a mechanical stable free-standing membrane and therefore a TFC membrane was an option. The P3HT had a weight average molar mass of $41 \text{ kg}\cdot\text{mol}^{-1}$ and a dispersity of 1.2.

3.2.2. Microporosities and gas separations

Nitrogen adsorption/desorption isotherms for the BT and the P3HT are plotted in Figure 1. The BET surface area was calculated to be $40.7 \text{ m}^2 \text{ g}^{-1}$ for the BT, and was found to be higher than the P3HT with a value of $25.7 \text{ m}^2 \text{ g}^{-1}$. The higher N_2 uptake capacity of the BT implies that it is more microporous than the P3HT. The sharp increase above 0.9 relative pressure (p/p_0) in both cases may be attributed to condensation of N_2 in the macropores and inter-particle voids.³ Although the BET surface area of the BT was higher than the linear P3HT, and is also comparable to another reported hyperbranched polythiophene ($\text{BET} = 58 \text{ m}^2 \text{ g}^{-1}$) synthesized via chemical oxidation;³ however, this is still low value for the BT to be yet considered as a porous material. The low value may be ascribed to a relatively low molar mass of the BT and consequently a lower branching degree.^{34,35} As the BT was readily soluble in common organic solvent, it was casted in membrane and a maximum CO_2/N_2 selectivity of 24 was recorded. This value is slightly higher to what was reported for linear regio-irregular poly(3-dodecylthiophene) (ri-P3DDT) ($\text{CO}_2/\text{N}_2 = 9.4$),¹² and is similar to the selectivity of linear rr-P3ATs.³⁶ It should also be mentioned that we had difficulty to get defect-free membranes. This could more likely be attributed to a poor mechanical stability of the BT membrane and the intrusion of the

less viscous polymer solution in the PI support as illustrated by the SEM cross-section image of the membrane in Figure 2.

Figure 1

Figure 2

3.3. Simulations

3.3.1. Characterization

Two conjugated polymers, P3HT and BT, were synthesized to investigate the influence of the macromolecular structure on the polymer microporosity. The former polymer, P3HT, had a linear structure while the latter, BT, was branched. In addition to experimental characterizations, simulations were used to calculate the adsorption behavior of the two polymers. For simplicity, the degree of polymerization for two polymers was set to 15. Specifically for BT, a degree of branching of approximately 62 % was assumed.

Comparing to linear P3HT, the branched polymer has higher quantities in all aspects due to irregular structure³⁵ as listed in Table 1. Simulated geometric accessible surface area (SA_{geo}) is visualized in Figure 3, which confirms that the branched structure could create more micropores inside the membranes rather than the linear P3HT.

Table 1

Figure 3

To better understand the adsorption process at the microscopic level, the geometric pore size distribution (PSD) for BT and P3HT was calculated and are shown in Figure 4. Both of the structures have their highest peaks close to 2 Å. Different from BT which produces a wider PSD, P3HT only has a sharp peak and its maximum pore size is about 4.5 Å. The vertical dash line in the figure indicates the diameter of N_2 probe (3.681 Å), which could predict that P3HT has a lower N_2 adsorption than BT.

Figure 4

3.3.2. Adsorption

The adsorption isotherms for BT and P3HT have been calculated by GCMC simulations (μVT ensemble). Temperature are fixed to 293 K, the pressure is varying from 1 to 20 bar with the increment equals 1. Figure 5 depicts the adsorption isotherms for BT and P3HT.

Figure 5

Table 2 lists the calculated diffusivity (D), solubility (S) and permeability (P), the first two quantities can be calculated by (6 and (5, furthermore, the product of D and S produces the permeability. For different gases in all aspects, BT has higher values than that of P3HT, which again proves that the hyperbranched structure has better gas-separation behavior than the linear counterparts.

For diffusivity, the trend for four gases in the BT is $O_2 > CO_2 > N_2 > CH_4$, P3HT has the same trend which means the complexity in polymer structure does not influence diffusivity behavior for different gases. The same conclusion could be found for solubility, but the trend for gases in the BT and the P3HT have different rule comparing to diffusivity, which is $CO_2 > CH_4 > O_2 > N_2$, such trend has excellent agreement to literatures.³⁷ As the product of D and S, permeability for gases in the BT and the P3HT has the same trend to that of solubility.

Table 2

To draw a brief conclusion based on simulation results, we can see that the complexity in polymer structure has huge influence on the gas-separation behaviors. Changing from linear to hyperbranched structure will significantly improve the performance of the gas-separation membrane. The higher BET surface area obtained by simulation may be attributed to an estimated higher branching degree of the simulated BT structure in comparison to the synthesized one.^{34,35}

4. Conclusions

By designing a 2,3'-bithiophene monomer and using a Pd(Ruphos) catalyst, we have successfully synthesized via a controlled chain growth polymerization a well-defined hyperbranched polythiophene (BT), which is CO₂/N₂ selective and has a higher BET surface area than the linear P3HT. This trend was confirmed by simulations of the geometric surface areas of the two polymer structures. Moreover, the BT is soluble in common organic solvents and can be readily processed in membrane for gas separation measurement, which is often difficult with most of reported hyperbranched CPs obtained via a chemical oxidative polymerization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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Scheme 1. Synthesis of the precursor monomer: i, CH_3MgBr , Ni(dppp)Cl_2 ; ii, NBS; iii, Pd(OAc)_2 , $\text{P(But)}_3\text{HBF}_4$, NaOH ; iv, NBS; v, I_2 , PhI(OAc)_2 .

Scheme 2. In situ monomer synthesis and polymerization mechanism of the BT: vi, $i\text{PrMgCl.LiCl}$; vii, ZnBr_2 .

Figure 1. N_2 sorption isotherms at 77 K of the BT (left graph) and the P3HT (right graph), adsorption (blue curve) and desorption (red curve).

Figure 2. Cross section SEM image of the BT composite membrane.

Figure 3. The geometric surface area for BT (left) and P3HT (right), green curves represent the polymer matrix and red space the geometric accessible surface area (S_{Ageo}).

Figure 4. Pore size distribution (PSD) for BT and P3HT at 293 K.

Figure 5. The adsorption isotherms for gases of interests at 293 K, BT (left) and P3HT (right).

Table 1. Porosity characteristics of the simulated BT and P3HT: geometric surface area (SA_{geo}), fractional free volume (f) and pore volume (V_{pore}).

Structures	$SA_{geo}/m^2 \cdot g^{-1}$	$\rho_{sim}/g \cdot cm^{-3}$	$V_{pore}/cm^3 \cdot g^{-1}$	f
BT	140 ± 15.8	1.14 ± 0.01	0.15 ± 0.01	0.21 ± 0.01
P3HT	6.70 ± 7.10	1.03 ± 0.01	0.06 ± 0.01	0.17 ± 0.01

Table 2. Calculated diffusivity (*D*), solubility (*S*) and permeability (*P*) values at 293 K and 1 bar, their units are $[10^{-8}\text{cm}^2/\text{s}]$, $[10^{-2}\text{cm}^3(\text{STP})/(\text{cm}^3(\text{polymer})\text{cmHg})]$ and [barrer], respectively.

Structures	CO ₂	CH ₄	N ₂	O ₂
BT ^D	15.8±6.74	3.57±1.97	9.027±4.24	25.6±10.4
P3HT ^D	3.67±1.81	0.577±0.355	1.83±0.988	6.25±2.98
BT ^S	29.3±3.98	9.39±1.46	2.38±0.355	4.20±0.520
P3HT ^S	3.31±0.765	0.576±0.299	0.123±0.077	0.455±0.150
BT ^P	464±3.98	146±1.45	37.1±0.355	66.3±0.520
P3HT ^P	13.1±8.43	0.393±0.383	0.272±0.275	3.12±2.28

^Ddiffusivity; ^Ssolubility; ^Ppermeability

A branched polythiophene (BT) is synthesized via a controlled polymerization and shows a higher microporosity ($\text{BET} = 40.7 \text{ m}^2 \cdot \text{g}^{-1}$) than the linear poly(3-hexylthiophene) (P3HT) ($\text{BET} = 25.7 \text{ m}^2 \cdot \text{g}^{-1}$). The same trend is confirmed by simulations, with the BT having a higher geometric surface area ($\text{SA}_{\text{geo}} = 140 \pm 15.8 \text{ m}^2 \cdot \text{g}^{-1}$) than the P3HT ($\text{SA}_{\text{geo}} = 6.7 \pm 7.1 \text{ m}^2 \cdot \text{g}^{-1}$). In addition, the BT membrane is gas selective, $\text{CO}_2/\text{N}_2 = 24$.

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Influence of branching of polythiophenes on the microporosity

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Influence of branching of polythiophenes on the microporosity

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1. Synthesis

The synthesis of the branched monomer **6** is depicted in Scheme S 1.

Scheme S 1. Synthesis of the precursor monomer: i, CH_3MgBr , $\text{Ni}(\text{dppp})\text{Cl}_2$; ii, NBS ; iii, $\text{Pd}(\text{OAc})_2$, $\text{P}(\text{But})_3\cdot\text{HBF}_4$, NaOH ; iv, NBS ; v, I_2 , $\text{PhI}(\text{OAc})_2$.

2. Characterization

2.1. ^1H NMR spectra

Bruker Avance NMR (300 MHz) was used to record the spectra of the synthesized compounds. The sample was dissolved in CDCl_3 and tetramethylsilane (TMS) was used as an internal standard.

Figure S 1. ^1H NMR spectrum of the compound **2**.

Figure S 2. ^1H NMR spectrum of the compound **3**.

Figure S 3. ^1H NMR spectrum of the compound **4**.

Figure S 4. ^1H NMR spectrum of the compound **5**.

Figure S 3. ^1H NMR spectrum of the precursor monomer 6.

2.2. GC-MS spectra

A Thermo Finnigan GC MS was used to determine the mass over charge (m/z) of the new compounds. The sample was dissolved in CHCl_3 and the solution was injected via a syringe in the apparatus.

Figure S 6. GC MS spectrum of the compound 4.

Figure S 7. GC MS spectrum of the compound 5.

Figure S 4. GC MS spectrum of the precursor monomer 6.