

Synthesis and Properties of Conjugated Microporous Polymers

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ABSTRAKT

Tato práce obsahuje stručný na příkladech založený teoretický popis různých mikroporéz-
ních polymerů a jejich aplikací v katalýze, separaci a skladování plynů, využití v senzo-
rech, bateriích, organické elektronice a kumulaci světelné energie. Dále práce obsahuje
popis modelových reakcí, jako jsou polykondenzace, cyklotrimerizace, cross-coupling a
řetězové polymerizace. V experimentální části najdeme (i) přípravu vybraných monomerů
a diskuzi k získaným výsledkům a (ii) přípravu polymerních sítí z několika monomerů 1,4-
diethynylbenzenu; 2,5-diethynyltiofenu; 2,7-diethynylfluorenu a post-polymerizační modi-
fikaci polymerů připravených z 1,4-diethynylbenzenu.

Klíčová slova: mikroporozita, konjugace, adsorpce, absorpce, separace, Sonogashira cross-
coupling, konjugované mikroporézní polymery, řetězová polymerizace, cyklotrimerizace,
polykondenzace, aromatické monomery, heterocykly

ABSTRACT

This work contains brief, example-based theoretical description of various microporous
polymers, their applications in fields of catalysis, separation and storage of gases, usage in
sensors, batteries, organic electronics and light-harvesting. Also contains description of
model reaction such as: polycondensation, cyclotrimerization, cross-coupling and chain-
growth polymerization. In the experimental part can be found (i) preparation of selected
monomers and discussion to obtained results and (ii) preparation of polymer networks
from various monomers, such as: 1,4-diethynylbenzene; 2,5-diethynylthiophene; 2,7-
diethynylfluorene and postpolymerization modification of the polymer from 1,4-
diethynylbenzene.

Keywords: microporosity, conjugation, adsorption, absorption, separation, Sonogashira
cross-coupling, conjugated microporous polymers, polycondensation, cyclotrimerization,
chain-growth polymerization, aromatic monomers, heterocycle

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CONTENTS

I	THEORETICAL PART.....	10
1	TYPES OF POROUS MATERIALS BY VARIOUS CRITERIA.....	11
1.1	POROUS MATERIALS BY COMPOSITION.....	11
1.1.1	Inorganic	11
1.1.2	Hybrids (MOF – Metalo-Organic-Frameworks).....	12
1.1.3	Organic (Polymers of intrinsic microporosity)	12
1.1.4	Covalent Organic Frameworks.....	13
1.1.5	Microporous Organic Polymers	13
1.1.6	Conjugated Microporous Polymers	14
1.2	MICROPOROUS MATERIALS BY SIZE OF PORES	14
1.3	POROUS POLYMERS/MATERIALS BY APPLICATION	15
1.3.1	Gas storage and separation.....	15
1.3.2	Catalysis.....	16
1.3.3	Light harvesting systems.....	16
1.3.4	Sensors	17
1.3.5	Organic electronics	18
1.3.6	Batteries	18
2	SYNTHESIS OF (CONJUGATED) MICROPOROUS POLYMERS.....	19
2.1	POLYCONDENSATION REACTIONS.....	19
2.1.1	Sonogashira cross-coupling as general procedure.....	20
2.1.2	Linear, branched and crosslinked structures via polycondensation	21
2.2	CHAIN-GROWTH POLYMERIZATIONS.....	22
II	EXPERIMENTAL PART.....	23
3	EXPERIMENTAL PART.....	24
3.1	CHEMICALS.....	24
3.2	MEASUREMENTS	24
3.2.1	Adsorption isotherms.....	24
3.2.2	NMR	24
3.3	SYNTHESIS OF MONOMERS	25
3.4	SYNTHESIS OF POLYMERS	27
4	DISCUSSION	29
4.1	SYNTHESIS OF MONOMERS	29
4.2	POSTPOLYMERIZATION MODIFICATION	30
4.3	SIMULTANEOUS POLYMERIZATION AND REACTIONS OF TRIPLE BONDS	33
4.4	UTILIZATION OF MONOMERS WITH MODIFIED BAND GAP	36
	CONCLUSION.....	41
	BIBLIOGRAPHY	42
	LIST OF USED SYMBOLS AND ABBREVIATION.....	46
	LIST OF PICTURES	47
	LIST OF TABLES	49
	LIST OF SUPPLEMENTARY DATA	50

INTRODUCTION

Conjugated microporous polymers (CMPs) belong to porous materials. Porous materials are those with significant portion of volume consisting of pores. [1] Pores are the voids in material which can be filled with either gas or liquid, remaining space is skeletal-like structure (framework) and can be considered also as the continuous phase. Porosity contributes to overall properties of material such as: its mechanical properties (rigidity vs. flexibility) and physical and chemical properties (conductivity, adsorption behaviour, hydrophilic or hydrophobic behaviour, etc.). Moreover, pores in material have high overall volume, and often the pore volume is higher than the volume of the continuous phase. Pore volume is maybe one of the most important aspects and is quantified as specific surface area, which is surface area related to weight unit (m^2/g).

I. THEORETICAL PART

1 Types of porous materials by various criteria

Similarly to ordinary linear polymers, divided by various criteria, the microporous polymers can be also divided by selected criteria. In particular we can discuss their composition and also size and distribution of pores, if we are taking their three dimensional structure in account.

1.1 Porous materials by composition

1.1.1 Inorganic

Zeolites (crystalline aluminosilicates and related materials) withstand catalysis under extreme conditions due their robust structure. Zeolites can be of the natural occurrence, but can be also prepared industrially. They are used for: petrochemical cracking, water softening and purification, natural zeolites don't have to be clean and can be contaminated by other minerals. Another advantage of industrial zeolites is that they can be tuned as to the desired properties. [2]

Silica is the term denoting material based on the silicon oxide with similar architecture to zeolites. [3] Silica materials differs from the zeolites by absence of aluminium in the structure. Contrary to zeolites, the framework of typical silica has no bronsted acid centres because there is no aluminium contained in the lattice. It is important e.g. in catalytic applications.

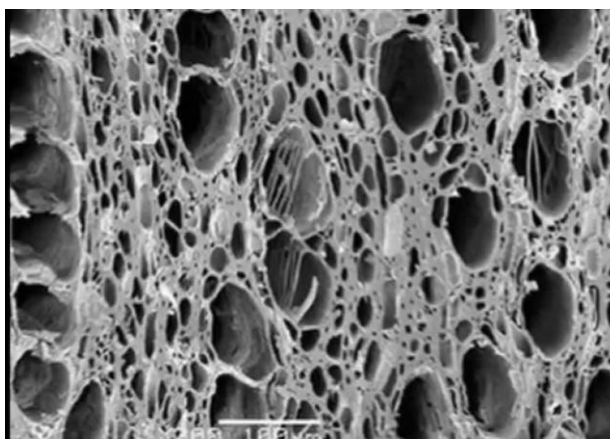


Figure 1: Activated carbon structure [4]

Activated carbon denotes for the special form of carbon with significantly extended surface area (up to 1500 m²/g). It is used in numerous applications like filtration, sorp-

tion of pollutants from the water of purification of alcoholic beverages or purification of chemicals in the synthesis of specialty polymers.

1.1.2 Hybrids (MOF – Metallo-Organic-Frameworks)

MOFs are inorganic metal ions or clusters of ions/atoms and organic units bonded together. Organic matter works as the connector with multiple functionality for the inorganic counterpart. The main use of MOFs lies in various types of catalysis and reversible gas sorption and separation. Structure of many MOFs sustains its microporosity after removal of solvent, other may collapse if solvent is evaporated and completely removed. Keeping structure stable even after the removal of solvent is essential for gas state catalysis and also for applications like gas separation and storage. [5]

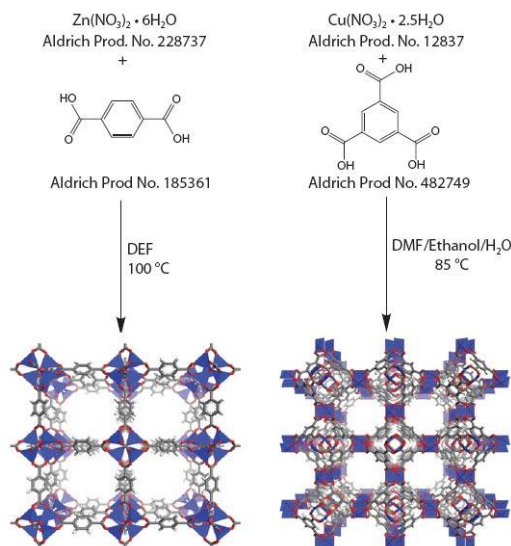


Figure 2: Scheme of synthesis of MOF. [6]

1.1.3 Organic (Polymers of intrinsic microporosity)

Polymers of Intrinsic Microporosity (PIM) are polymer-based organic microporous materials whose microporosity comes from inability to organize polymer chains into densely packed structure due to size and steric effects (geometry) of main chain units. PIMs can be prepared in two variants, as insoluble networks or soluble polymers. (MOPs with this type of microporosity are soluble in organic solvents whereas after precipitation, micropores will restore.) Both these variants behave analogously to other conventional microporous materials. One of the uses of soluble PIMs may be highly selective gas separation through membranes, for this application we need to process it to thin film. PIMs

have potential to be used also in hydrogen storage, membrane separation processes or heterogeneous catalysis. [7][8]

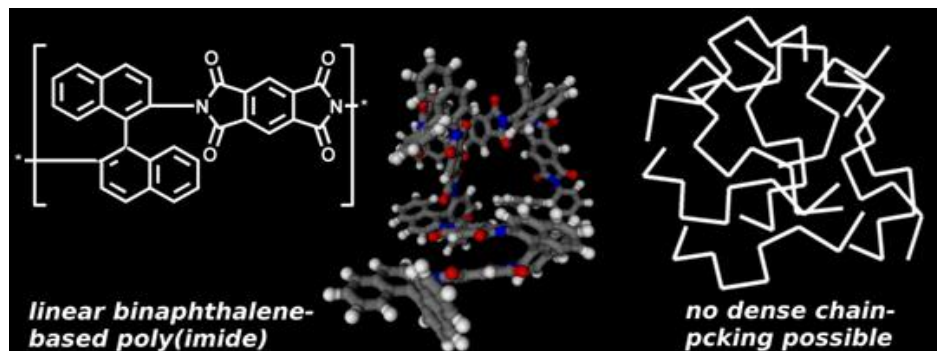


Figure 3: Example of PIM. [9]

1.1.4 Covalent Organic Frameworks

Covalent Organic Frameworks are well defined crystalline structures with permanent microporosity, usually made of light elements such as: H, B, C, N and O bonded together by covalent bonds. Synthesis of COF through molecular building blocks would bring covalent frameworks with possibility to functionalise them into lightweight materials suitable for gas storage, photonic and catalytic reactions. [10]

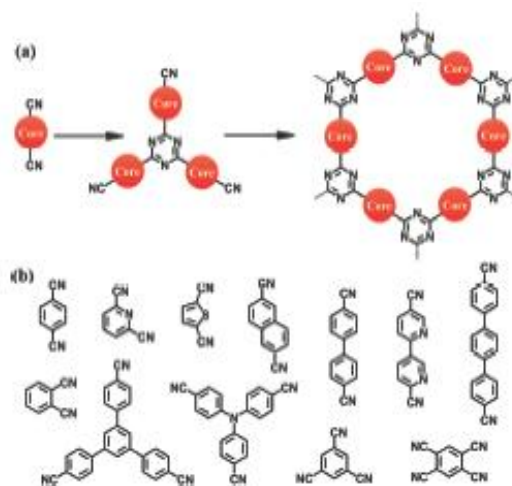


Figure 4: example of COFs prepared by cyclotrimerization reaction. [10]

1.1.5 Microporous Organic Polymers

Microporous Organic Polymers [11] are new type of porous polymers with possible applications in catalysis, opto-active materials and sensors. They might have strong chemical resistance, can be synthesized by various methods and their chemical properties and

structural and texture parameters can be modified. Also one of their advantages is low specific density that signalizes high specific surface. One subclass of MOP is group of conjugated microporous polymers.

1.1.6 Conjugated Microporous Polymers

Conjugated microporous polymers CMPs [12]. are organic microporous polymers, which are built up from numbers of C-C bonds and/or aromatic rings or heterocycles, forming conjugated network. CMPs are main topic of this work and will be evaluated in next chapters according to theoretical reviews and practical experiments done in laboratory. Advantage of CMPs (and other types of porous materials as well), is ability to customize its attributes to suit application in which they will be used.

1.2 Microporous materials by size of pores

Another criterium to differentiate among porous materials is to recognise them by the size of its pores. We divide porous materials into three groups by their pore size:

Tab. 1: microporous materials divided by size of pores

type of porous material	size of pores in nm:
microporous	<2
mesoporous	(2- 50)
macroporous	>50

It is important to notice that very often are present pores of two or all three types (micro-mesoporous and micro-meso-macroporous materials). Distribution of pores, their size, shape and volume is correlated to the synthesis method utilized in the synthesis of microporous polymer and take part in each application in which we want them to perform. Having a material with uniform pore size can lead to better application properties; zeolite is as an example. Gas separation ability of zeolite comes directly from its uniform-sized pores that will let only molecules with corresponding size to flow through the network. Ability to separate molecules of gases is most likely limited by the distribution of pore sizes. Porosity is a function of the molecular structure rather than, for example, polymer

materials formed by templating methods. It is presence of micropores which lead to very high apparent surface areas that are observed in some nanoporous polymers. Micropores also contribute most to the adsorption of sorbate molecules at lower pressure. As mentioned above, absolute specific surface of porous materials is mainly given by size and amount of micropores, this statement can be proven by simple calculation, if a cube with a side length of $a = 1\text{ cm}$, then its surface $S = 6 \cdot 10^{-4} \text{ m}^2$. Having pores with size of 1 mm and with approximation that their walls are infinitesimally thin, cube would contain 10^3 pores, each with surface of $6 \cdot 10^{-6} \text{ m}^2$, the final specific surface would be $6 \cdot 10^{-3} \text{ m}^2$. If the pores is shortened to 1 nm , then the cube would contain $1 \cdot 10^{21}$ of pores with apparent surface of $6 \cdot 10^{-18} \text{ m}^2$, the absolute specific surface would be 6000 m^2 . Micropores may be present as a consequence of intrinsic structure (PIMs) or due to hypercrosslinking (extensive cross-linking) of structures which also wouldn't have microporosity in any other way.

Having solid materials with micropores is impossible without having fraction of mesopores. Mesopores can be described as inter-particle void and their origin comes from reaction mechanism and conformation. We can hardly synthesize continuous microporous phase. Of course also mesoporous materials exist e.g. mesoporous silica (see above).

Macropores are important also in the microporous and micro/mesoporous materials. Generally, macropores allow stored, separated or catalysed compound easily access the micropores and mesopores. If the material has such architecture we can call it hierarchical.

1.3 Porous polymers/materials by application

Porous polymers do have a lot of interesting applications. Some of them will be introduced in this chapter, based on applications demonstrated on experiments from given literature. The idea is to show capabilities of CMPs and point out some specifics of their usage.

1.3.1 Gas storage and separation

Gas sorption, storage and separation of N_2 , H_2 , CO_2 , CH_4 or other gases or vapours is one of the most important applications. Adsorption is a consequence of surface energy i.e. the electronic structure of the atoms and molecules present on the surface, atoms in bulks of solid are bounded together at all sides by each other, however atoms at the surface are bound incompletely and are more reactive and attractive for gases, vapours and liquids

due van der Waals forces present to balance atomic forces. Here the CMPs and MOPs in general take advantage over other adsorbents due their immensely high surface area and ability to chemically tune their structure to selectively adsorb specific gases. For instance, selectivity of sorption of CO₂ can be tuned by introducing the heteroatoms into the microporous networks. [13]

1.3.2 Catalysis

CMPs were tested as photocatalysts e.g. by Dr. Zhang et al. [14] Ability of CMPs to produce singlet oxygen was evaluated with dispersion of cross-linked polymer containing α -terpinene. Dispersion was mixed with oxygen and put through photoreactor, where it was exposed to blue light with the wavelength 420 nm. Analysis of substrate conversion was done with ¹H NMR spectroscopy. Conversion rate of reaction was proportional to surface area. Polymer with lowest surface area (270 m²/g) reached conversion of 26 % and polymer with 660 m²/g achieved conversion of 96 %. Conversion of α -terpinene to ascaridole can be seen in fig. 5. This example demonstrates the advantages of microporous polymers over non-porous materials.

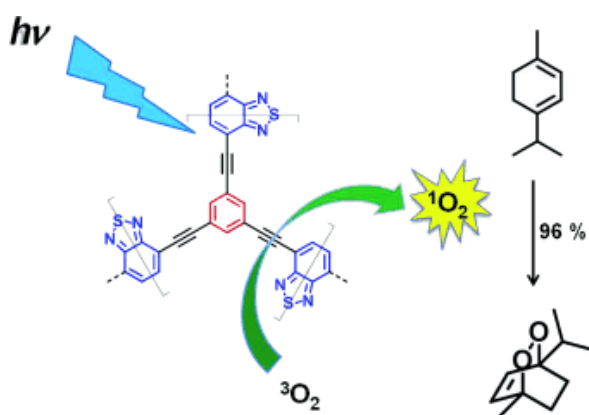


Figure 5: Example of utilization of CMP in the catalysis (oxidation of α -terpinene). [14]

1.3.3 Light harvesting systems

Example of light-harvesting system utilizing CMPs was published recently. [15] In described case is used phenylene microporous matrix with surface slightly above 1000 m²/g with adsorbed coumarin dye, which can easily enter pores. Coumarin also forms donor-acceptor pair with microporous network. In this case it was proven, that luminescence of coumarine dye was 21 times more intensive than it was when coumarin was excited alone.

Emission of microporous carrier and light harvester is minimized by non-radiative transitions and energy transfer.

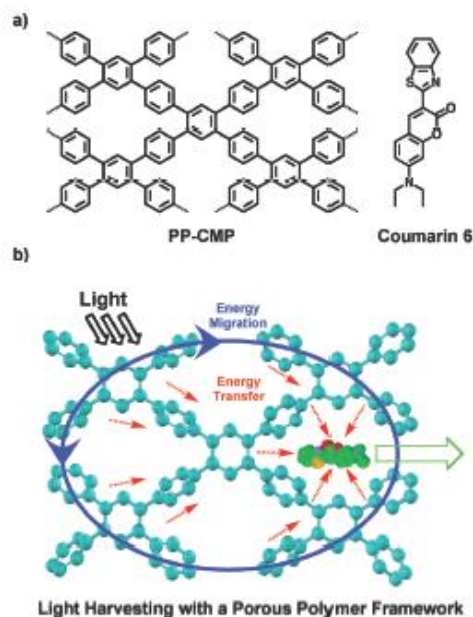


Figure 6: Schematic representation of light-harvesting system utilizing the CMP. [15]

Point of light-harvesting systems is gathering light energy and its transfer to proper substrate. CMPs have advantage in having distinctive absorption themselves and also they can spatially confine molecules of dyes. This ability is advantage for photochemical processes that are many times more effective with isolated molecules.

1.3.4 Sensors

Soluble linear conjugated polymers are already used for detection, but CMPs have some attributes that make them a little superior. One of them is possibility of higher number of contacts of analyte with active material due its large surface. The problem with CMPs in this application is the form of the product. There are reported CMPs based on the phenylcarbazole [16] and are generally synthesised in its usual form, i.e. powder; however for sensor application it is better to have the active material as a thin film. Way of processing CMPs to thin films and retaining their proprieties is preparing them via electropolymerization with concurrent polymer film deposition. Electropolymerization even allows controlling thickness of these films. This thin film then lets other attributes to emerge, porosity, extended π conjugation and high rate electron transfer. In the presented example, the CMP sensors have outstanding selectivity and sensitivity in chemo and bio-sensing. It

should be noted that not all the CMPs can be prepared by the electropolymerization. For example thiophene-based polymers are also suitable for the electropolymerization. [17]

1.3.5 Organic electronics

Conductivity and/or inherent conjugation are important properties given to CMPs due π -conjugation and makes them candidates for the prospective applications in organic electronics. Disadvantage of using CMPs in electronic devices is same as mentioned in subchapter before – more complicated processability. Nevertheless, this can be overcome through electropolymerization as well. Demonstration of possibility to use CMPs in organic electronics was done in polymer light-emitting diodes (PLEDs), using CMP films as interlayer on anode. This PLED was then compared to two other diodes, one containing undoped CMP as interlayer and second without CMP interlayer. The doped CMP device had a turn-on voltage at 2,2 V with maximum brightness of 33 000 cd/m², luminous efficiency of 20,7 cd/A, that is 51% better than undoped CMP and 37% better than PLED without CMP. [18]

1.3.6 Batteries

A study of utilization of CMPs as electrochemical capacitors was done. CMPs were modified to sandwich-like nanosheets, using graphene as the basic template forming the composite G-CMP. These G-CMPs were then worked up by pyrolytic conversion to produce hierarchically porous carbon nanosheets. This material was tested as a supercapacitor and showed a 48% increase in capacitance than porous carbon without graphene additive. G-CMP sheets may be used as both small-current collectors and long-distance charge transportation units during charging/discharging, utilizing high electrical conductivity of graphene. Hierarchical pore structure could possibly improve ion injection or extraction. Improved electron transport should shorten the average charge transport distance, leading to the better capacitance and energy storage capacity. [19]

2 Synthesis of (Conjugated) microporous polymers

2.1 Polycondensation reactions

Most usual reaction for CMP preparation is the polycondensation. For example, reaction used for preparation of cross-linked MOP is:

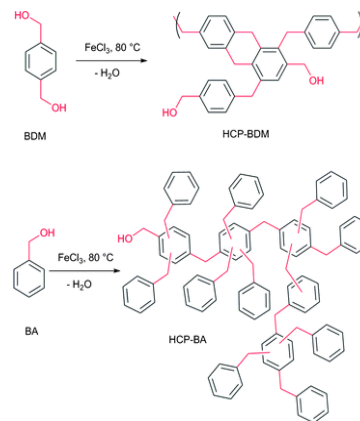


Figure 7: Synthesis of microporous polymer via Friedel-Crafts crosslinking reaction. [20]

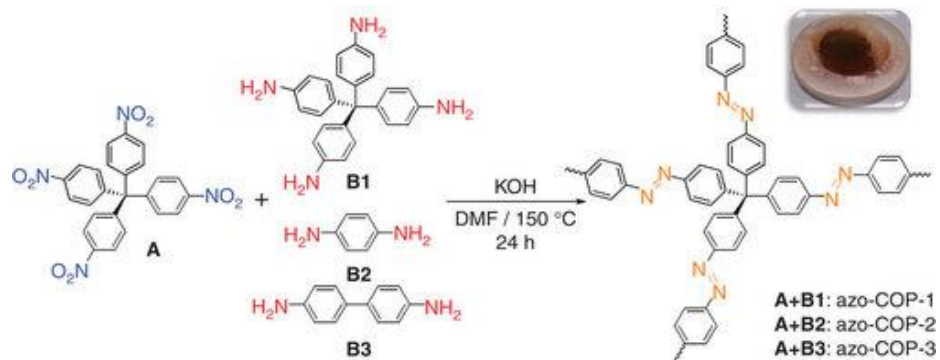


Figure 8: Preparation of MOP linked via azo groups. [21]

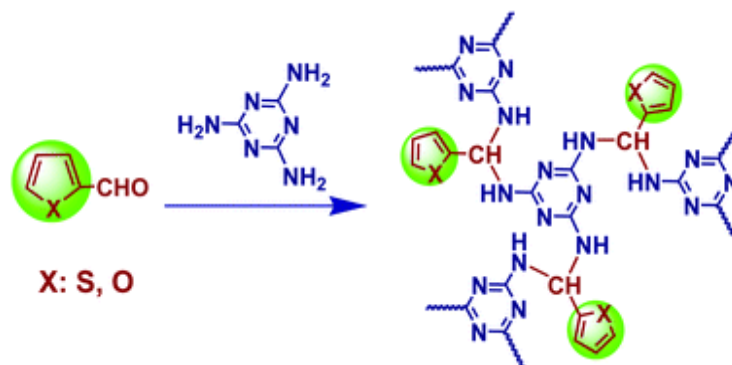


Figure 9: Preparation of MOP by the non-catalysed reaction – formation of aminals. [22]

Obviously it's possible to use conventional polycondensation with high rate of conversion and yields, reaction that can work with monomers with various functionalities to prepare microporous polymers. Example of these reactions may be synthesis of polymers based on melamine, where second reactant is di, tri or multi-aldehyde.

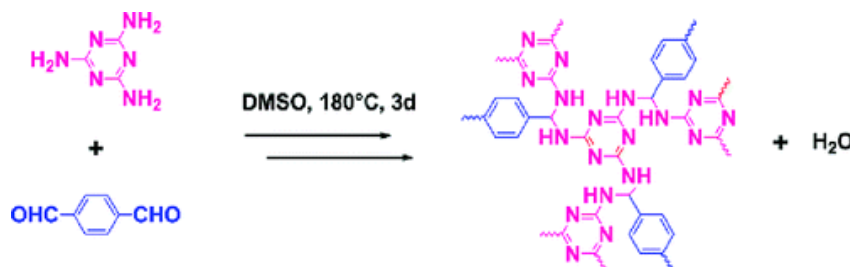


Figure 10: Synthesis of melamine based microporous polymer. [23]

For synthesis of CMPs it's necessary to use catalysed reactions because formation of aryl-aryl or aryl-heterocycle bonds is otherwise almost impossible to be done. Typical example of reaction can be seen in figure 11. Derivate of fluorene with multiple functionality is copolymerized with bifunctional derivate while forming the network. Reaction of this type is called Suzuki Coupling and uses palladium catalysed reaction of halogenderivates with boric acid derivative.

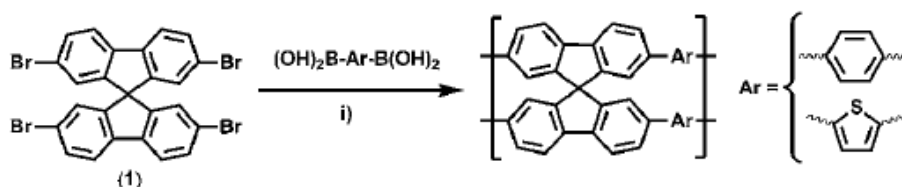
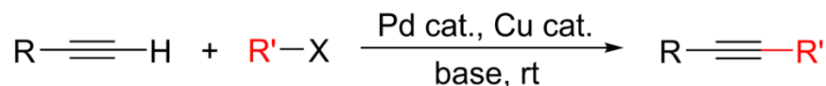


Figure 11: Preparation of CMP by Suzuki coupling [24] Polycondensation reactions of acetylenes

2.1.1 Sonogashira cross-coupling as general procedure



R' = Aryl, Vinyl
X = I, Br, Cl, OTf

Figure 12: General Sonogashira reaction scheme

The Sonogashira reaction is a cross-coupling reaction between terminal alkyne and organohalide, forming C-C bonds. It uses Palladium catalyst, copper catalyst and base. Reaction begins with oxidative addition of organohalide to Pd(0), forming Pd(II) complex.

Another step is transmetalation with organo-copper that is made from terminal alkyne and copper catalyst. Then halide on the palladium complex is replaced with alkyl anion and regenerates the copper halide catalyst. Desired product is then given to us by reductive elimination, which also regenerates palladium catalyst and after this step, reaction cycle is ready to be restarted. Of course Sonogashira reaction is suitable not only for the polymerization but also as the reaction of post-polymerization modification. Some advantage is that it proceeds under mild conditions and thus suitable also for the utilization of more sensitive compounds.

2.1.2 Linear, branched and crosslinked structures via polycondensation

Aromatic acetylic monomers with two ethynyl groups, i.e. diethynylarenes are known for decades as initial compounds, from which is possible to prepare soluble linear conjugated oligomers and polymers with various covalent structure, dependent on type of non-chain-growth polymerization. [25][26] Example is shown in figure 13

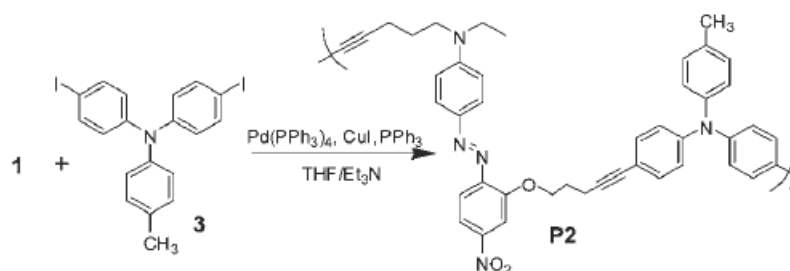


Figure 13: Example of utilization of acetylene derivatives for the preparation of linear polymers. [26]

If the functionality of acetylene and/or halogenide derivative is increased, we can obtain the (hyper)cross-linked materials as shown in the Figure 14

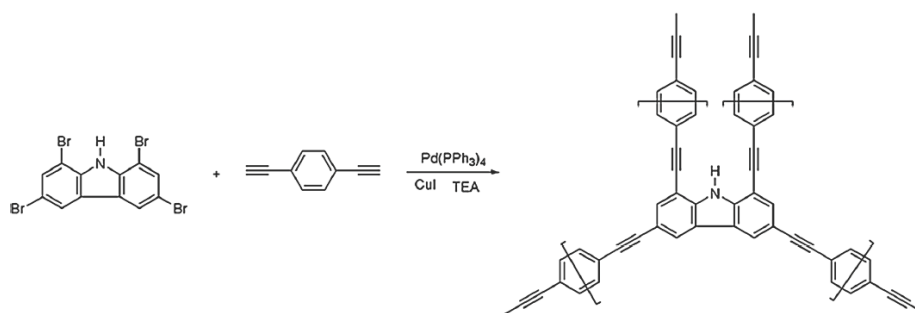


Figure 14: Synthesis of microporous polymer based on the carbazole and 1,4-diethynylbenzene by Sonogashira cross-coupling reaction.[27]

Alternative reaction of triple bonds is cyclotrimerization. [28] Figure 15 shows typical reaction. Three triple bonds forms one benzene ring substituted in positions 1,3,5 or 1,2,4 depending on several factors. This reaction leads to more conjugated system in which the building units are connected via stable benzene ring instead of polyene units.

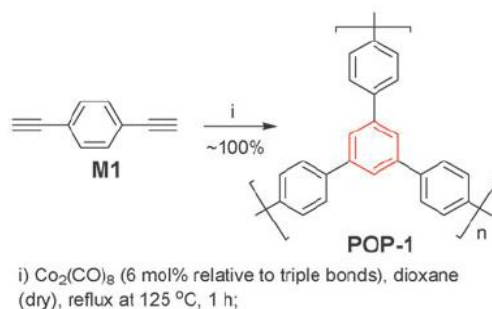


Figure 15: Cyclotrimerization leading to the microporous network. [28]

2.2 Chain-growth polymerizations

Another relevant reaction is the utilization of chain-growth polymerization. In case of monosubstituted acetylenes the application of Rh-based insertion catalyst leads to the (often) soluble polymers called monosubstituted polyacetylenes. [29]



Figure 16: preparation of linear polyacetylene.

This material represents conjugated analogy of polystyrene. Main chain of the polymer is composed of alternating single and double bonds. We can take alternative monomer with one single triple bond. In such molecule the triple bond is internal. It is also possible to polymerize into the linear polymer but it is called disubstituted polyacetylene [30] and requires also chain-growth polymerization but in this case it is co called metathesis catalyst. If we take monomer with two (or more) triple bonds we can apply also chain-growth polymerization catalyst but due to the increased functionality of the monomer we can obtain material from branched to highly cross-linked. [31] This approach represents conjugated analogy of divinylbenzene. See Figure 16.

II. EXPERIMENTAL PART

3 Experimental part

3.1 Chemicals

1,4-diethynylbenzene (DEB), norbornadiene acetyl acetonato rhodium(I), 2,5 diiodothiophene, trimethylsilylacetylene, triphenylphosphine, bis(triphenylphosphine)palladium(II) dichloride, piperidine, 4-iodobenzylamine were purchased from Sigma Aldrich. Tetrahydrofuran (THF), dichloromethane (DCM), copper(I)iodide, methanol, hexane, LiAlH₄, NaOH, these chemicals were purchased from LaChema. THF was distilled from LiAlH₄, all the other chemicals were used as received. 2,7-Dibromofluorene and 2,7-Dibromofluoren-9-one were synthesised according to literature procedures by Dmitrij Bondarev.

3.2 Measurements

3.2.1 Adsorption isotherms

These measurements were performed on BELsorp- mini II. Absorbed gas was nitrogen. Results were analysed with BEL Master™ analysis software. Sample preparation and measurement: At first the sample is cleansed of already present atmospheric air and/or adsorbed solvents. The cleansing process is done by applying combination of heat and vacuum (3 hours, 100°C, and vacuum ≤ 1 Pa). Solid is then cooled under vacuum, in our case to 77K and after this step, an adsorptive N₂, is dosed to the solid in specific doses. After each addition of gas, pressure is let to balance itself to make calculation of adsorbed quantity possible.

3.2.2 NMR

Solution spectra were recorded on the Varian UNITY^{INOVA} 400 operating at 400 MHz in CDCl₃. ¹H NMR spectra were referenced using tetramethylsilane (TMS) as the internal standard. The ¹³C cross-polarization magic-angle spinning (CP/MAS) ssNMR spectra of the polymers were obtained at 14.1 T (600 MHz NMR JEOL JNM-ECA600II NMR spectrometer). Finely powdered samples were placed into 3.2-mm zirconia rotors and the measurements were performed under the MAS frequency of 12 / 20 kHz at room temperature.

3.3 *Synthesis of monomers*

2,7-Bis[(trimethylsilyl)ethynyl]fluorene, DEF-Si

This was one stage reaction with Sonogashira cross-coupling mechanism (see Fig. 17). As reaction vessel we have used Schlenk tube, in which we had 950 mg (2,82 mmol) of 2,7- dibromofluorene dissolved with 5 ml of THF and added 1 ml (7,03 mmol) of ethynyltrimethylsilane. Another step was addition of catalytic system compounds for Sonogashira reaction. We used 70,2 mg (0,1 mmol) of PdCl₂(PPh₃)₂, 19,04 mg (0,1 mmol) CuI, 26,23 mg (0,1 mmol) PPh₃, 0,2 ml of piperidine. All compounds were dissolved and mixed with remaining 5 ml of THF. Reaction mixture was heated to 45°C overnight. After cooling and evaporation of the THF the solid was redissolved and some small amount of activated charcoal was added. System was then passed through short silica column, solvent evaporated and the obtained solid was used as obtained. Yield (709 mg, 68 %)

NMR: ¹H NMR (400 MHz, CDCl₃, 25°C, ppm): 7.74-7.44 m (6H, arom, fluorene), 3.86 s (2H, -CH₂-), 0.27 s (18H, -Si(CH₃)₃) See spectrum in the Supplementary information

2,7-Diethynylfluorene, DEF

661,3 mg of DEF-Si (1,844 mmol) was added together with 147,52 mg of NaOH (3,688 mmol) to 25 ml of CH₃OH in round-bottom flask and it was stirred at laboratory temperature overnight. Methanol was evaporated and residue was dissolved in DCM and run through short silica column. Purity was checked by TLC and subsequently by NMR. Isolated yield was 295,5 mg, that is 74,8%.

NMR: ¹H NMR (400 MHz, CDCl₃, 25°C, ppm): 7.77-7.45 m (6H, arom, fluorene), 3.87 s (2H, -CH₂-), 3.13 s (2H, -C≡CH) See NMR spectrum in the supplementary information part.

2,7-Bis[(trimethylsilyl)ethynyl]fluoren-9-one, DEFON-Si

It was one stage reaction similar to DEF-Si, as a reaction vessel we have used Schlenk flask in which we first weighted 2,7-Dibromofluoren-9-one (1400 mg, 4 mmol), catalytic system (We used 70,2 mg (0,1 mmol) of PdCl₂(PPh₃)₂, 19,04 mg (0,1 mmol) CuI, 26,23 mg (0,1 mmol) PPh₃) without PdCl₂(PPh₃)₂, 0,2 ml of piperidine and approximately 10 ml of freshly distilled THF. We dissolved compounds, and then added PdCl₂(PPh₃)₂ together with 1,44 ml of ethynyltrimethylsilane (10.2 mmol, 2.5 equivalents). Schlenk

flask was put into oil bath heated to 50°C and stirred for 48 hours. Reaction mixture was then evaporated and after redissolving in THF passed through short SiO₂ column. Organic matter was evaporated and the solid washed with ethanol and dried. Isolated yield 500 mg (33 %) **NMR:** ¹H NMR (400 MHz, CDCl₃, 25°C, ppm): 7.74-7.44 m (6H, arom. fluorene), 0.27 s (18H, -Si(CH₃)₃). See NMR spectrum in the Supplementary information part.

2,5-Bis[(trimethylsilyl)ethynyl]thiophene, DET-Si

2,5-Diiodothiophene (3.35 g = 10 mmol) was dissolved in freshly distilled THF and placed into the Schlenk tube. Catalytic system, 28,6 mg (0,15 mmol) CuI, 39,5,mg (0,15 mmol) PPh₃ and 105 mg (0,15 mmol) PdCl₂(PPh₃)₂ dissolved in 10 ml of THF with 0,2 ml of Piperidine was added subsequently and then ethynyltrimethylsilane was added (3,15 ml = 22,35 mmol). Reaction was heated to 35-40 °C under stirring overnight. Reaction mixture was poured into water, extracted with DCM and passed through silica and crystallized from EtOH after evaporation of the solvent on the rotary evaporator. Yield: 2,15 g (78%). **NMR:** ¹H NMR (400 MHz, CDCl₃, 25°C, ppm): 7.05 s (2H, thiophene), 0.26 t (18H, -Si(CH₃)₃). See NMR spectrum in the Supplementary information part. Purity is similar to another portion of the 2,5-Bis[(trimethylsilyl)ethynyl]thiophene prepared previously. Batches were combined.

2,5-Diethynylthiophene, DET

2,5-Bis[(trimethylsilyl)ethynyl]thiophene (2.76 mg = 10 mmol) was dissolved in methanol (20 ml) and NaOH (800 mg = 20 mmol) was added. Reaction mixture was stirred at laboratory temperature overnight. Then the reaction mixture was poured into the 100 ml of water and extracted with DCM. Solvent evaporated and material stored in the fridge. TLC showed one product. Yield: 1,2 g (91%). **NMR:** ¹H NMR (400 MHz, CDCl₃, 25°C, ppm): 7.13 s (2H, thiophene), 3.36 s (2H, -C≡CH). See NMR spectrum in the Supplementary information part.

3.4 Synthesis of polymers

Poly(DEB)-P-1

1st stage of reaction, chain-growth insertion polymerisation

Polymerisation was performed for 3 hours at 70°C. As a reactor we used small screw-cap ampoule with volume of 20 ml. At first we weighted 189 mg (1,5 mmol) of DEB and dissolved it in 1,5 ml of DCM in ampoule and then 13,3 mg (0,045 mmol) of catalyst Rh(acac)(nbd), already dissolved in 0,5 ml of DCM was added. The first stage was terminated by replacing of DCM by THF via washing over in the sintered-glass filter. Attention was paid to keep polymer in the swollen state. After extensive washing we consider polymer as free of DCM and main part of Rhodium catalyst. Polymer precursor was then ready for use in the second stage. Approximately 25% of precursor was separated and dried.

2nd stage Sonogashira cross-coupling postpolymerization modification

All the reactants and all compounds of catalytic system: polymer precursor, 4-iodobenzylamine (236 mg = 1,01 mmol), Bis(triphenylphosphine)palladium(II) dichloride (35,5 mg = 0,05 mmol), Copper(I) iodide (6,20 mg = 0,033 mmol), triphenylphosphine (13,1 mg = 0,056 mmol), Piperidine (0,5 ml = 5 mmol) were dissolved in THF and added to the polymer precursor. Overall reaction volume was approximately 8 ml. Reaction mixture was heated at 40°C for 48h under mild stirring. Quenched reaction mixture was washed with THF until colour disappeared and no signs of organic material were visible on TLC plate with UV indicator. Elemental analysis: 77,57% ; 66,41% ; 63,71% C; 4,65% ; 3,96% ; 3,67% H; 1,32% ; 1,13% ; 1,08% N

Poly(DEB)-P-2

This reaction was performed similarly with Poly(DEB)-P-1 except the 1st stage in which we used 6 ml of DCM, which lead to slower reaction kinetics, swelling has arisen subsequently. We also separated 25% of precursor. Elemental analysis: C: 80,51; 80,04; 76,58; H: 4,78; 4,73; 4,42; N: 1,44; 1,43; 1,37

Poly(DEB)-Sim

189 mg 1,4-DEB (1,5 mmol), 233 mg (1,5 mmol) 4-iodobenzylamine, 31,5 mg Pd(PPh₃)₂Cl₂, 3,75 mg CuI, 13,1 mg PPh₃, was placed into the screw cap ampoule and dis-

solved in mixture of 5 ml of DCM and 1 ml of freshly distilled THF and 0,2 ml of piperidine. Then we added 13,3 mg Rh(nbd)(acac). Reaction was performed at 45°C for 48 hours. After the reaction was terminated, the product was successively washed with DCM, THF and CH₃OH in order to remove all unreacted or soluble matter. Yield was 130 mg. Elemental analysis C: 77,8%; 78,24%; 78,25%; H 5,04%; 4,99%; 5,01% N: 3,28%; 3,30%; 3,34%

Poly(DEF)

107 mg (0,5 mmol) of 2,7-diethynylfluorene was dissolved in 1,5 ml of DCM and placed into the screw-cap ampoule. Then the catalyst Rh(nbd)(acac) 4,41 mg (0,015 mmol) dissolved in 0,5 ml of DCM was added and the reaction mixture was placed in the preheated bath. Reaction was performed for 72 hours at 70 °C. Final product was washed of catalysts in glass filter with THF. After evaporation of THF, product yielded 101,8 mg (95%) and was moved to vial for storage.

Poly(DET)-C

1,06 g (8 mmol) of 2,5-diethynylthiophene was dissolved in 12 ml of DCM. Part of the monomer was not dissolved in DCM and thus it was separated and worked up parallelly (see Poly(DET)-T). With addition of Rh(nbd)(acac) (64 mg = 0,218 mmol) reaction mixture was inserted into oil bath at 70°C for 48 hours. After reaction was completed, we again washed product with THF and let it dry. Product yield was 800 mg, which might be almost 100% of theoretical yield

Poly(DET)-T

Some amount of 2,5-diethynyl thiophene, roughly 150 mg, was polymerized without catalyst, as it started to polymerise while it was in storage. It did not hold its liquid form and transformed into gel. This part of monomer was dissolved in ethylene-glycole and inserted into oil bath with same conditions as Poly(DET)-C. Another handling with product was same as with the Poly(DET)-C. Yield: 145 mg (almost quantitative, no leaching from the solid during its work-up on the sintered glass filter)

4 Discussion

4.1 Synthesis of monomers

For verification of possibility of chain-growth polymerization we have used commercially available monomer 1,4-diethynylbenzene. This compound is used abundantly. But for following polymerizations we had to prepare monomers on our own. First synthesis was preparation of the 2,7-diethynylfluorene. Direct introduction of terminal triple bond is close to unreal. Because of that, procedure using Sonogashira coupling had to be used, to introduce triple bond protected by trimethylsilyl (see figure 17). This compound is more stable. Trimethylsilyl group can be removed easily by reacting with base if necessary. Three protected monomers were prepared and two of them then de-protected and used in polymerization. It is observed, that 2,7-Diethynyl-9H-fluorene is rather stable compound and similarly to 1,4-diethynylbenzene, only mild degradation occurs while storing the sample. Most likely the degradation is caused by spontaneous cyclotrimerization. Situation is different with 2,5-diethynylthiophene. Protected 2,5-Bis[(trimethylsilyl)ethynyl]thiophene is also relatively stable compound. De-protected diethynylthiophene starts to change its colour right away and after some hours, degraded product starts to appear (even at lowered temperature). It's presumably due the fact that 2,5-diethynylthiophene is liquid. This, together with different electron structure might cause higher reactivity of triple bond. Geometry of the molecule might also take part in the lower stability. Reactivity of 2,5-DET is also discussed in the scope of polymerization. Another monomer we have chosen was the 2,7-diethynylfluorene-9-on. We managed to prepare protected monomer, but its de-protection was let unfinished due the lack of time.

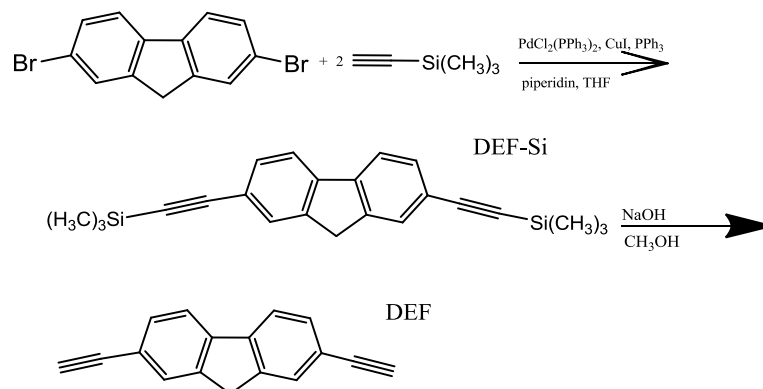


Figure 17: Preparation of 2,7-bis(trimethylsilyl)ethynylfluorene and 2,7-diethynylfluorene

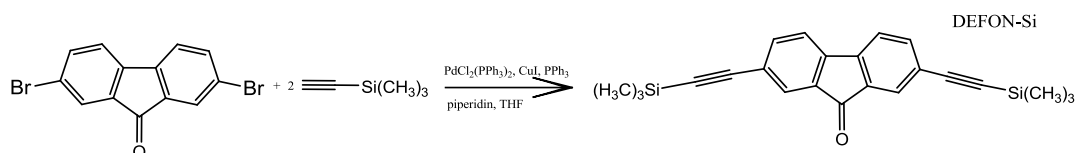


Figure 18: Preparation of 2,7-bis(trimethylsilylethynylfluoren-9-one) and 2,7-diethynylfluorene.

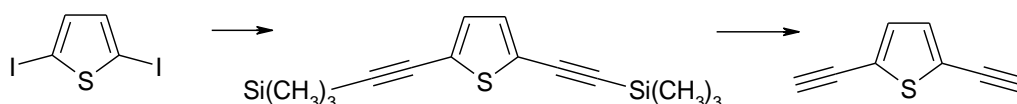


Figure 19: Synthesis of 2,5-bis(trimethylsilylethynyl)thiophene (DET-Si) and 2,5-diethynylthiophene (DET).

4.2 Postpolymerization modification

First phase of reaction is the chain-growth polymerization leading to hypercrosslinked material. That way, usability of such reaction was verified for preparation of microporous polymer. Withdrawals from the reaction mixture before beginning of the second stage are proving that even in relatively diluted system, intense networking and creation of the large surfaces occurs (see Tab. 2). Usability of the reaction for analogous aromatic monomers just as heterocyclic monomers was also verified (see chapter 4.4). From chapter 4.3 it's clear, that the used chain-growth catalyst is stable enough and allows polymerization in presence of another catalytic system.

Synthesis of Poly(DEB)-P-1 and Poly(DEB)-P-2

In this case we are executing polymerisation up to certain stage, then the polymerisation is terminated and another reaction, polymer analogous modification on the precursor network is done. These are two consecutive reactions; the first one is chain-growth polymerisation, leading to creation of network. The Second reaction is modification of said network with Pd-catalysed “cross-coupling” reaction.

For polymerisation of 1,4-DEB (1,4-Diethynylbenzen) with chain-growth mechanism we know, that it is possible to obtain quantitative or almost quantitative conversion and very high surface area (up to 1469 m²/g) [31]. On the other hand, system still contains unreacted triple bonds which are suitable substrates for some selected reactions such as Sonogashira coupling.

Shortening of reaction time leads to lowering of reaction conversion and probably also to higher volume of unreacted triple bonds. Another fact is that many triple bonds are reacting while system is precipitating. Meaning that lowering volume of gel composed of the formed polymer network brings functional groups closer together in a way that couldn't be possible in the swollen gel state (in which the polymerisation takes place) but only when the solvent is removed during the precipitation or drying. Note that this leads to creation of rigid bonds that permit the material to swell to same size as before precipitating. It is the result of properties of the polymerization catalyst. Rhodium based complex used in the polymerization is stable at the variety of temperatures, in various solvents and environments, even in air. On the other hand, many of palladium-based catalysts are quite sensitive to some solvents and aerial oxygen.

Analysis of adsorptions shows, that in networks made of 1,4-DEB, pores are most likely truly microporous and sub-micropores (unreachable to molecules bigger than gasses) make up relatively small volume from overall pore volume.

According to this information, it looks like better solution to keep polymer in swollen gel form and change the solvent for consecutive reaction. In case, that we dry the material and then again swell it, the size of pores will be smaller and it would make the accessibility for next reactants as worse as for the catalytic system, which is made up from relatively bulky molecules.

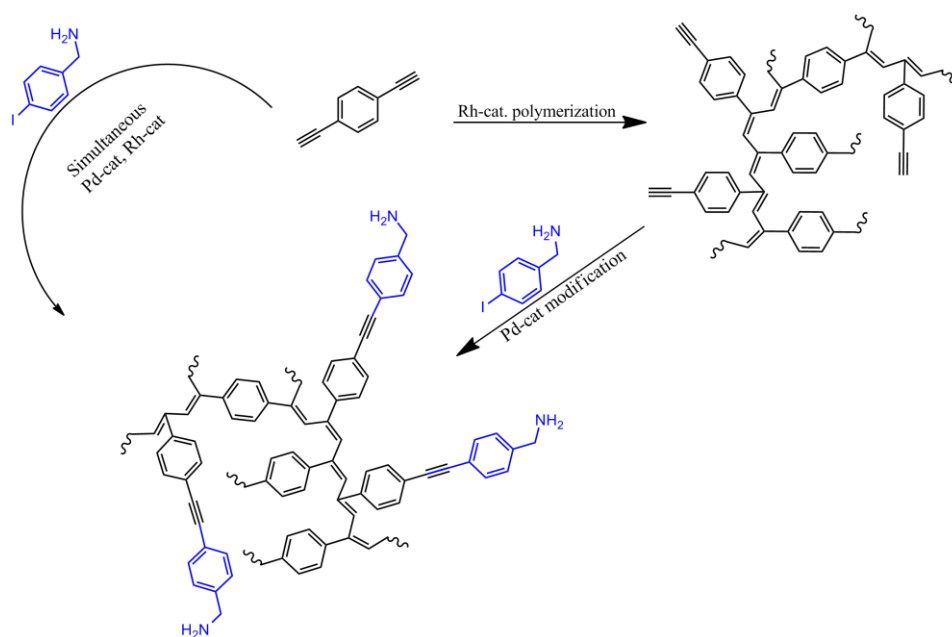


Figure 20: Synthesis of Poly(DEB) polymers.

Results are at the Fig. 21. We can see that sample Poly(DEB)-P-1 has rather higher surface. It is noticeable that the surface is only slightly lower than that achievable in the polymer precursor. Therefore, the modification with benzylamine does not change the porosity of the material. Poly(DEB)-P-2 exhibits little bit larger surface and the difference from its precursor is very small. It indicates that the execution of the reaction in the more swollen gel is slightly beneficial to the second stage – modification reaction. Pores in the precursor are more accessible to the compounds of the second catalytic system and resulting in slightly higher nitrogen content. We cannot make some strong statement about the comparison of Poly(DEB)-P-1 and -2, respectively. However, interesting feature is the higher overall pore volume for both the samples occurring simultaneously with the decrease in the surface. This might be attributed to more significant ratio of mesopores or bigger micropores caused by the steric action of benzylamine moieties contrary to the unsubstituted Poly(DEB). Meaning that purely microporous material has larger surface but the overall pore volume is lower in contrary to the micro/mesoporous material which has less micropores (resulting in lower surface) but the overall volume is bigger.

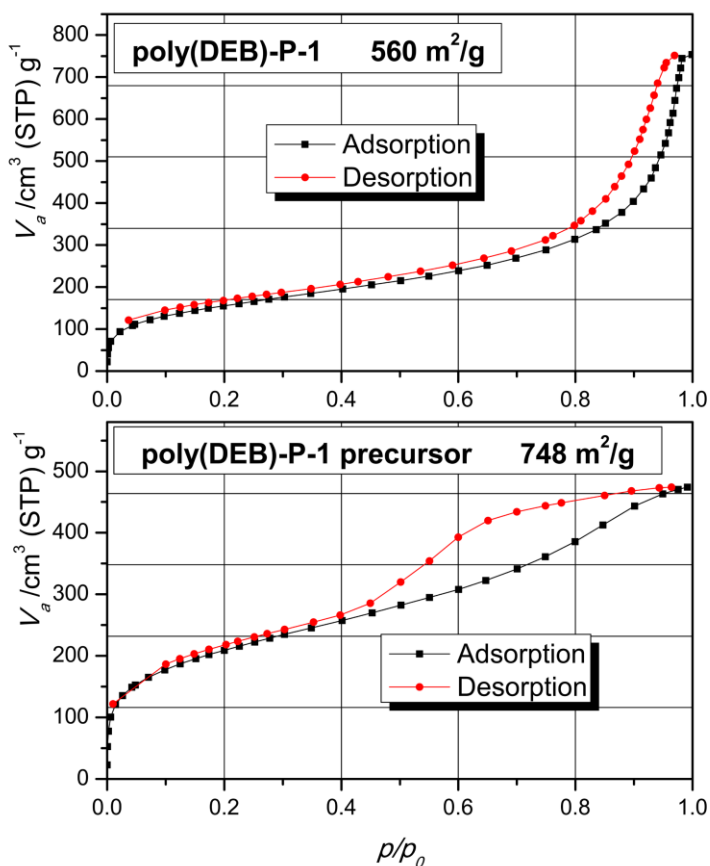


Figure 21: Adsorption and Desorption isotherms of poly(DEB)-P-1 and its precursor.

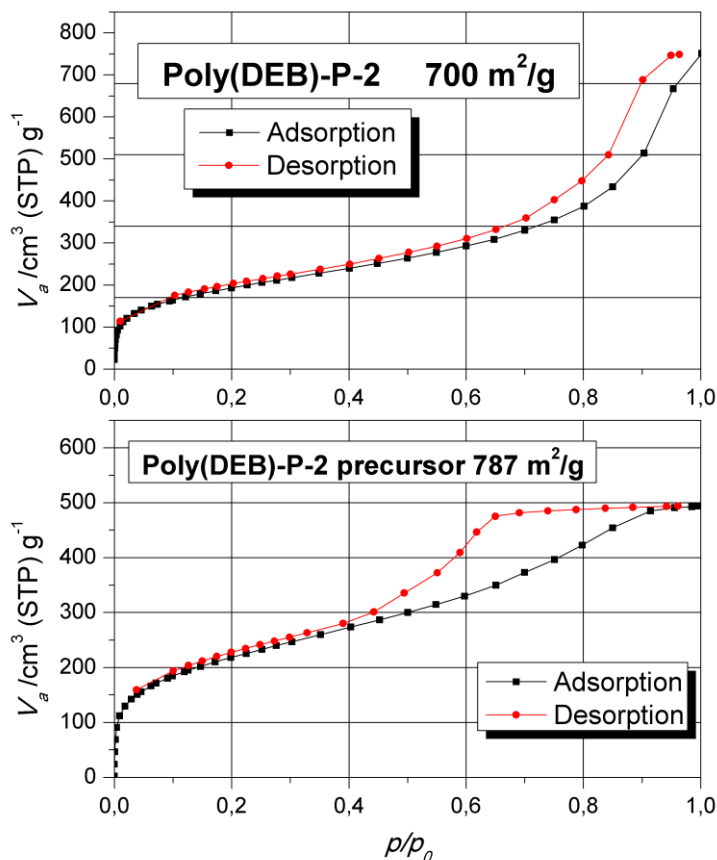


Figure 22: Adsorption and desorption isotherms of poly(DEB)-P-2 and its precursor.

4.3 Simultaneous polymerization and reactions of triple bonds

Synthesis of Poly(DEB)-Sim

In this synthesis we are trying to accomplish two stages of previously performed reaction simultaneously, opposite to previous attempts in synthesis of Poly(DEB)-P-1 and Poly(DEB)-P-2, which was done consecutively. This means executing chain-growth polymerisation together with Sonogashira polycondensation at once. We are trying to test the compatibility of these two reactions in the first place.

After each reaction, it is needed to slightly change the conditions (namely solvents and temperature). For example THF, successfully used in Sonogashira coupling is utterly unusable solvent for network growth, chain-growth polymerization of 1,4-diethynylbenzene in THF gave only marginal porosity. [31]

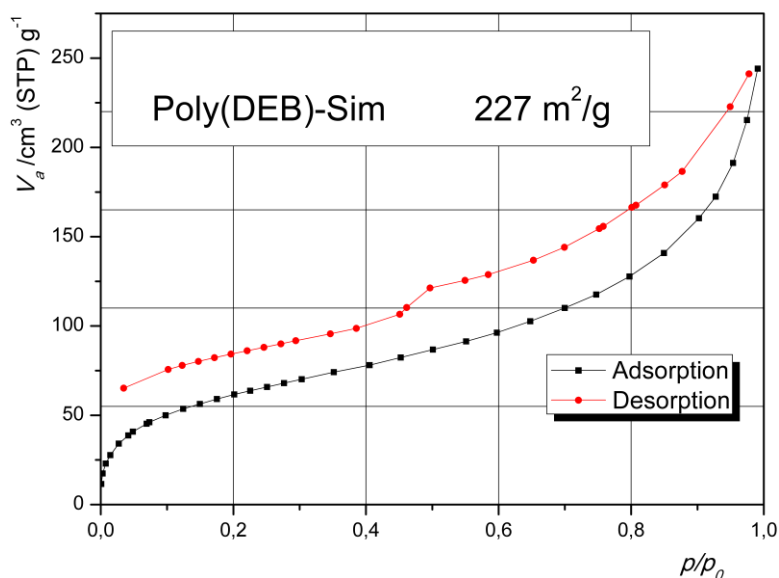


Figure 23: BET isotherm of the sample Poly(DEB)-Sim

We have chosen the ratio of reactants 1:1, which equals to ratio of triple bonds to iodine groups 2:1. This was meant to assure enough bonds for both reactions. Considering, that the starting network growth limits mobility, it should also decrease the probability of reacting of both triple bonds at one common benzene core. If proceed, this would create particle, which can't join the growing network. On the other hand, thanks to presence of huge reactant and parts of catalytic system, we have big probability that not all triple bonds will react, because they won't get close together in the way effective enough.

Smaller surface of Poly(DEB)-Sim in comparison to Poly(DEB)-P-1 and Poly(DEB)-P-2 may point out the fact, that when one bulky group bonds onto monomer, the whole reaction is directed to less branched chains, which are easily put together. Another explanation is ordinary closing of pores.

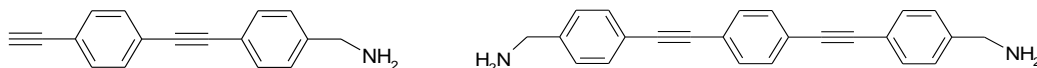


Figure 24: Possible structures prepared by the Sonogashira reaction proceeding simultaneously with the polymerization.

Similar influence of bulky side groups was observed in copolymerisation before. [32]

Content of implemented amino groups in Poly(DEB)-P-1 and Poly(DEB)-P-2 was not exceptionally high, we have managed to raise the amount of nitro groups in Poly(DEB)-Sim, but at cost of surface area (see table 2). Implementation of amino groups may seem to be even bigger problem than we thought.

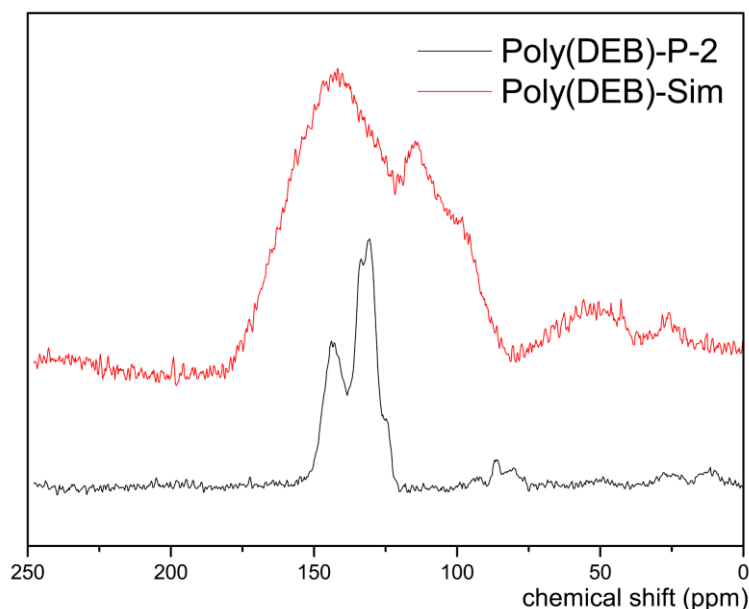


Figure 25: NMR spectra of Poly(DEB)-P-2 and Poly(DEB)-Sim.

ssNMR spectra of samples Poly(DEB)-P-2 and Poly(DEB)-Sim are shown on Figure 25. Both samples have fairly good rendered benzene cores and polyene structures – exactly what triple bonds should be transformed into during the polymerisation (150-120 ppm) and it is possible to detect signals from non-reacted triple bonds (75-90 ppm). However, signal of methylene CH₂ group from bonded benzylamine isn't observed. We assume, that nitrogen proven by elemental analysis isn't contained in aminogroups, but that it has transformed into other structures. Solid state NMR measurement is itself complicated and in comparison to solution spectrums it has gradually lesser signal resolution. Copper, that's used as a co-catalyst have probably played its role in our case. We didn't manage to properly wash it away and its stand behind lower quality of our spectrums because copper ions are paramagnetic.

Table 2: Compositions of prepared polymers, BET surface area, pore volume and nitrogen content in samples modified with

sample	Composition of compounds in reaction mixture	BET surface [m ² /g]	Overall pore volume [cm ³ /g]	Nitrogen content by EA
poly(DEB)-P-1	1,4-diethynylbenzene + 4-iodobenzylamine	560	1.15	1,1%
poly(DEB)-P-2	1,4-diethynylbenzene + 4-iodobenzylamine	699	1.13	1,4%
Poly(DEB)-Sim	1,4-diethynylbenzene + 4-iodobenzylamine	227	0.37	3,3%
Poly(DEF)	2,7-diethynylfluorene	799	1.18	n/a
Poly(DET)-C	2,5-diethynylthiophene	859	0.73	n/a
Poly(DET)-T	2,5-diethynylthiophene	309	0.41	n/a
poly(DEB)-P-1 precursor	1,4-diethynylbenzene	748	0.73	n/a
poly(DEB)-P-2 precursor	1,4-diethynylbenzene	787	0.76	n/a

4.4 Utilization of monomers with modified band gap

Raising capacity in CO₂ capture or shifting the band-gap (position of the edge of absorption spectrum and of course both HOMO and LUMO levels, respectively) or red shift of the overall spectrum of polymer can be done by tuning covalent structures of polymer itself in the chain-growth polymerization itself, what is more defined method than post-polymerisation modification. It was shown, that incorporation of heteroatoms [13] can substantially enhance the selectivity for carbon dioxide as well as its simple adsorption. It is known from the conjugated-polymers chemistry that the increase in the aromaticity or change the band gap of the polymer leads to the red shift in absorption characteristics.

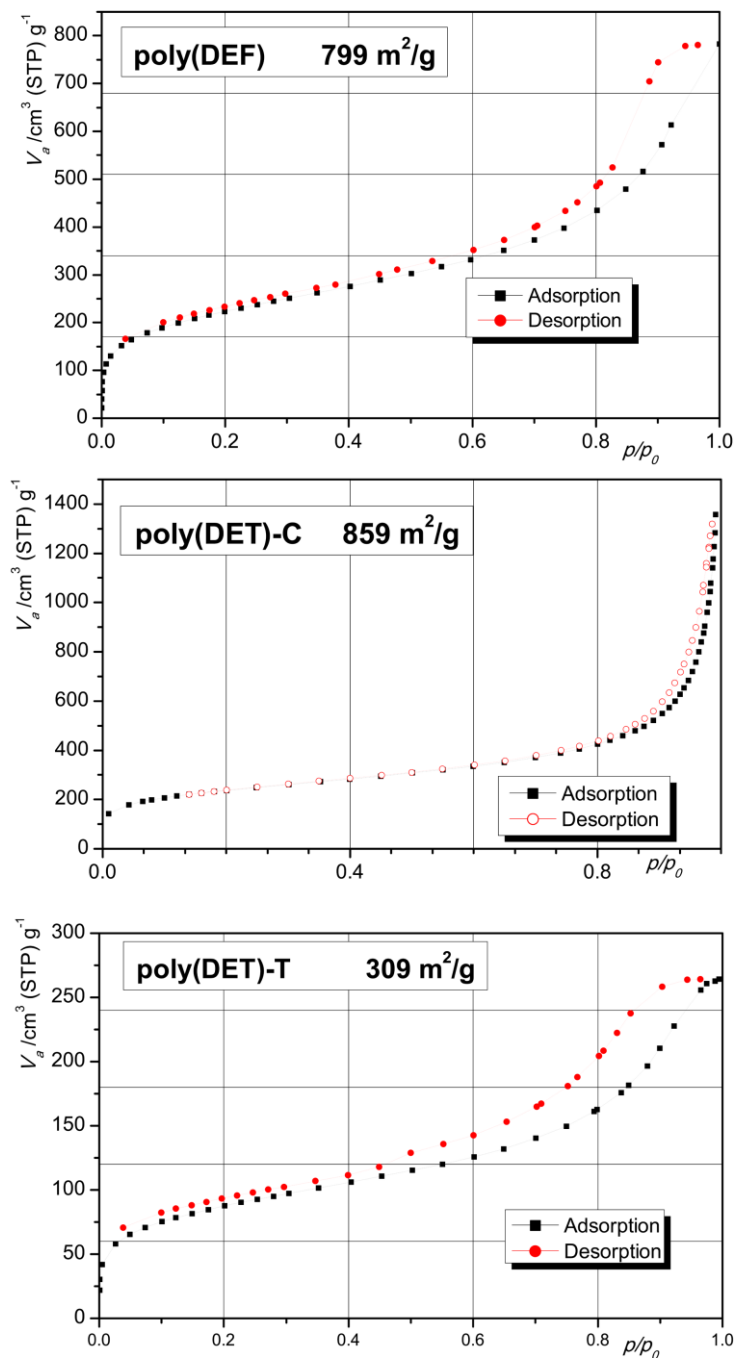


Figure 26: BET isotherms of Poly(DEF), Poly(DEF)-C and Poly(DEF)-T

We selected two approaches. First approach is extending of conjugation by replacing used monomer with another one, which has lower band gap. We decided to test replacement of benzene with fluorene. Shifting from phenylene groups of the main chain to the fluorene main-chain groups in linear conjugated polymers, is followed by moving absorption band edge from 400 nm in polyparaphenylene to 480 nm in polyfluorene. [33]

Poly(DEF)

Synthesis of Poly(DEF) proceeded smoothly without complications and we managed to obtain almost quantitative yield of polymer. We observed slightly darker colour than poly(DEB) but we haven't performed detailed spectroscopic investigation. Spectra of absorptions of powders have to be measured as diffused reflectance and equipment for this measurement was not available. We can only guess that this polymer has lowered band gap. However, polymer seems to be as microporous as poly(DEB) precursors. BET isotherm indicates the micro/mesoporous character of the polymer.

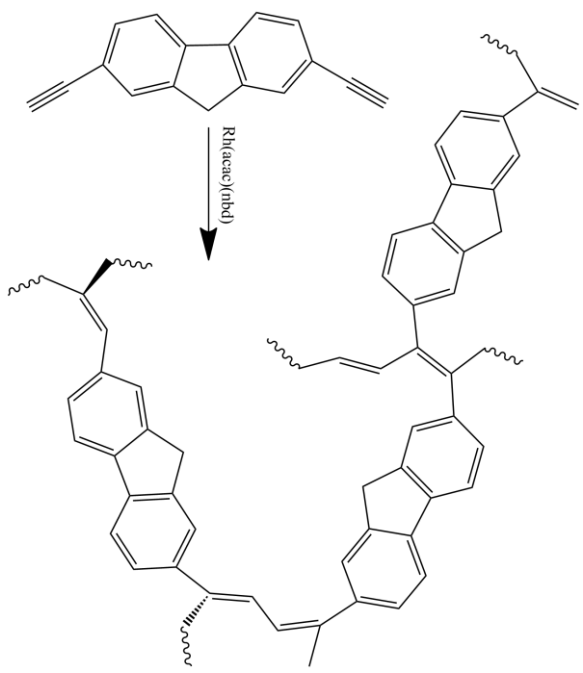


Figure 27: Reaction scheme of DEF polymerization

Poly(DET)

Second approach is the utilization of selected heterocycle. Thiophene can be considered as an analogue of phenylene and even fluorene but with much lower band gap and possibility of synthesis much more conjugated systems. Shift in the absorption edge in hundreds of nanometres [34] is again showing us similarity in the comparison of linear polyphenylene or polyfluorene.

Polymerization itself proceeded well, but we observed complications with the monomer. As mentioned before, we are able to see degradation of the monomer. Therefore we observed insoluble (gel like) part of the monomer which was not utilized in the catalysed reaction but it was worked up in parallel experiment.

Catalysed polymerization was performed in the same manner as Poly(DEB) samples. Polymerization started immediately. Final product was gel-like structure which collapsed in the course of washing into the dark-brown powder. When we compare Poly(DEB) and Poly(DET) we can see significant difference in colour (see figure 29) which surely reflect the lower band gap of thiophene-based materials. Overall surface is over 800 m²/g which is considered high value. Therefore we can conclude that chain-growth polymerization is suitable also for selected heterocycles and provides large surfaces.

Parallel to the catalysed polymerization we performed thermal polymerization. In case of 1,4-diethynylbenzene we can obtain products based on cyclotrimers and oxidized monomers which are not porous. In case of 2,5-diethynylthiophene we obtained insoluble porous powder material. BET analysis revealed surface above 300 m²/g which is much lower than in case of catalysed polymerization but high enough to attribute it to the extensive crosslinking. This sample has also micro/mesoporous character. We do not have any plausible explanation except the geometrical one in combination with higher reactivity. Thiophene units are refracted and can reach more space (take rotation into account) and meet more units to react with.

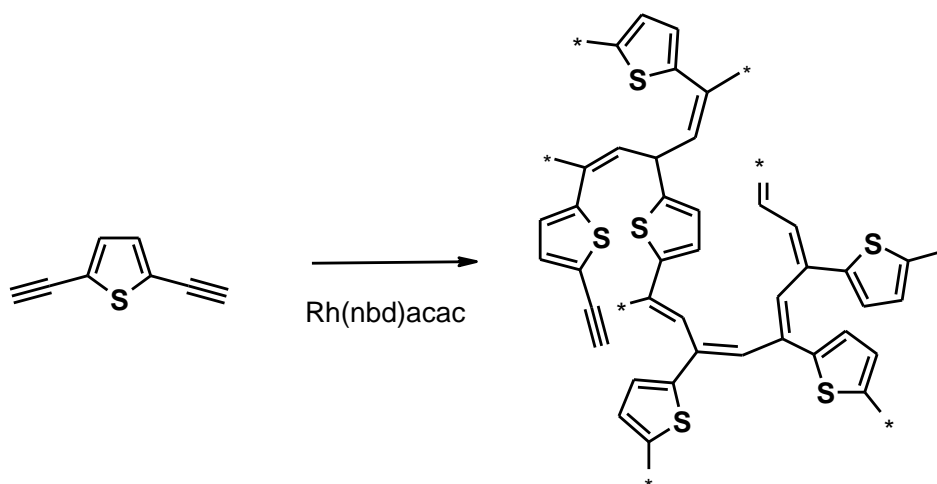


Figure 28: scheme of DET polymerization



Figure 29: *difference in colour between Poly(DEB) and Poly(DET)*

CONCLUSION

In this work we describe and discuss (i) synthesis of monomers (ii) testing chain-growth polymerization in preparation of microporous polymers and (iii) postpolymerization modifications of finished polymer networks.

Two monomers were prepared and tested as a monomers for chain-growth polymerisation. These monomers were 2,7-Diethynyl-9H-fluorene and 2,5-Diethynylthiophene. The second one shows as less stable, most likely because this monomer is liquid compound, and in combination with different electron structure, triple bonds are more reactive. Third tested monomer was 1,4-diethynylbenzene. It was polymerised with use of chain catalyst and prepared networks were then modified. We have managed to prepare two polymers with content of nitrogen by bonding iodobenzylamine through Sonogashira cross-coupling. This is a two stage reaction, after first stage we have extracted approximately 25% of mixture (for comparison) and the rest was used for second stage, Sonogashira cross-coupling. In conclusion was observed that modification with 4-iodobenzylamine changes surface area only slightly, see figures 21 and 22 and table 2.

Simultaneous reaction (polymerisation and modification) was then tested on Poly(DEB)-Sim. This reaction was successful in scope of raising content of nitrogen in network and its functionality at cost of surface area. This loss of surface may be explained by closing of pores or creation of less branched chains that are folding more easily.

Utilization of monomers with modified covalent structure was performed in polymerisation of Poly(DEF), Poly(DET)-C and Poly(DET)-T. Two ways of this modification can be done, extending conjugation by replacing benzene with fluorene – Poly(DEF) and utilization of heterocycle – Poly(DET). It was shown that 2,7-diethynylfluorene is possible to prepare by chain-growth polymerisation. In case of Poly(DET) we prepared two polymers, by catalysed polymerisation it was Poly(DET)-C with surface area over 800 m²/g, which points at conclusion that chain-growth polymerisation is also available for heterocycles. Second material was Poly(DET)-T, surface area of 300 m²/g, was prepared by non-catalysed thermal polymerisation. This increased reactivity might be due to high reactivity combined with steric factors.

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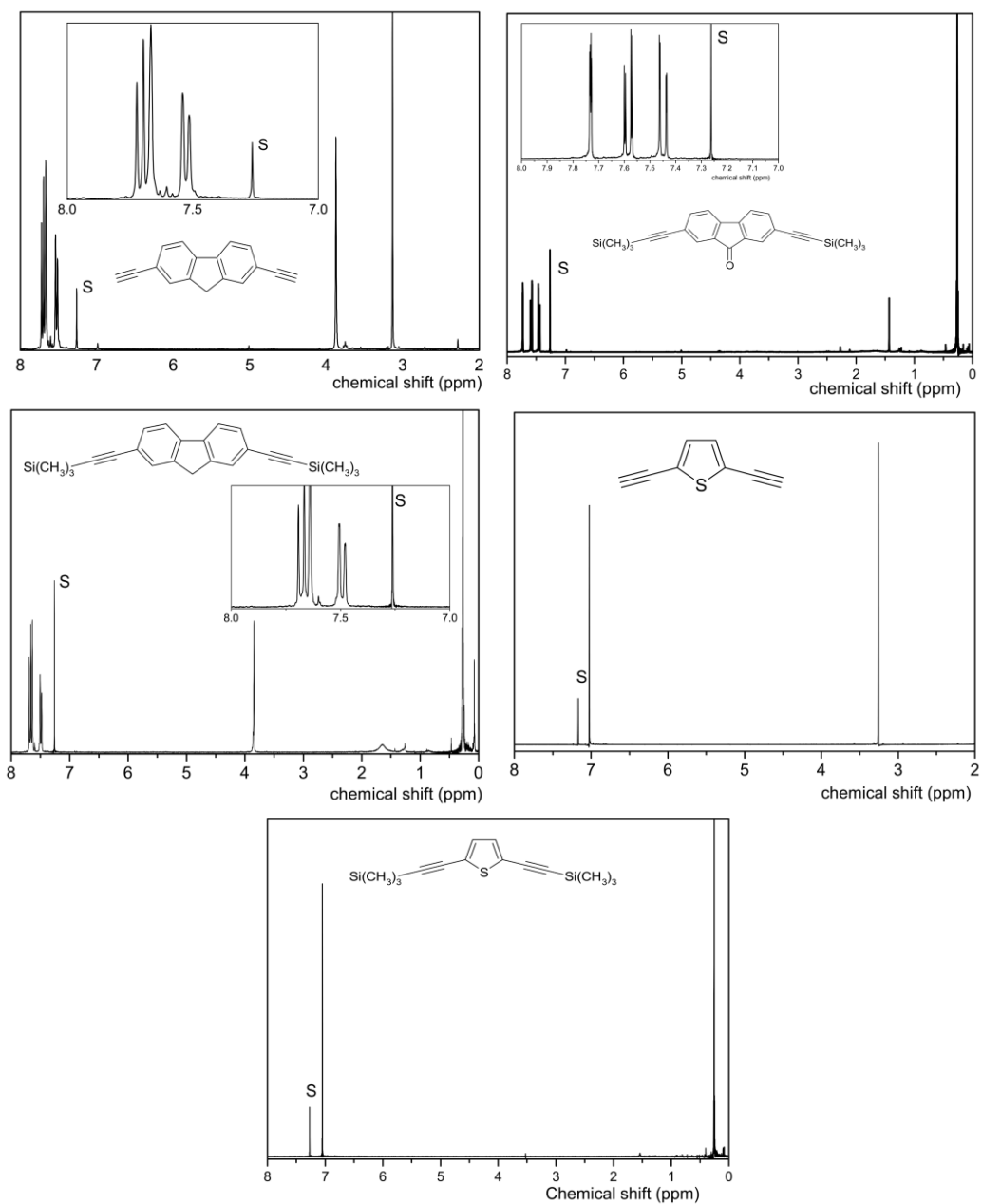
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SUPPLEMENTARY DATA:

Supplementary data A: NMR spectra of protected and de-protected monomers prepared in laboratory

LIST OF USED SYMBOLS AND ABBREVIATION

CMP	Conjugated microporous polymer
MOP	Microporous organic polymer
COF	Covalent organic framework
PIM	Polymer of intrinsic microporosity
MOF	Metallo-organic Framework
DCM	Dichloromethane
THF	Tetrahydrofuran
Rh(acac)(nbd)	Norbornadiene acetylacetonato rhodium (I)
PLED	Polymer light-emitting diode
G-CMP	Graphene-based conjugated microporous polymer
HOMO	Highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
BET	Brunauer, Emmett, Teller method of measuring surface area
NMR	Nuclear magnetic resonance
ssNMR	Solid-state Nuclear magnetic resonance

LIST OF PICTURES

Figure 1: Activated carbon structure [4]	12
Figure 2: Scheme of synthesis of MOF [6]	13
Figure 3: Example of PIM [9]	14
Figure 4: example of COFs prepared by cyclotrimerization reaction [10]	14
Figure 5: Example of utilization of CMP in the catalysis (oxidation of α -terpinene) [14]	17
Figure 6: Schematic representation of light-harvesting system utilizing the CMP [15]	18
Figure 7: Synthesis of microporous polymer via Friedel-Crafts cross-linking reaction [20]	20
Figure 8: Preparation of MOP linked via azo groups. [21]	20
Figure 9: Preparation of MOP by the non-catalysed reaction – formation of aminated. [22]	20
Figure 10: Synthesis of melamine based microporous polymer. [23]	21
Figure 11: Preparation of CMP by Suzuki coupling [24] Polycondensation reactions of acetylenes	21
Figure 12: General Sonogashira reaction scheme	21
Figure 13: Example of utilization of acetylene derivatives for the preparation of linear polymers. [26]	22
Figure 14: Synthesis of microporous polymer based on the carbazole and 1,4-diethynylbenzene by Sonogashira cross-coupling reaction.[27]	22
Figure 15: Cyclotrimerization leading to the microporous network	23
Figure 16: preparation of linear polyacetylene	23
Figure 17: Preparation of 2,7-bis(trimethylsilyl)ethynylfluorene and 2,7-diethynylfluorene	30

Figure 18: Preparation of 2,7-bis(trimethylsilylethynylfluoren-9-one) and 2,7-diethynylfluorene.	31
Figure 19: Synthesis of 2,5-bis(trimethylsilylethynyl)thiophene (DET-Si) and 2,5-diethynylthiophene (DET).	31
Figure 20: Synthesis of Poly(DEB) polymers.	32
Figure 21: Adsorption and Desorption isotherms of poly(DEB)-P-1 and its precursor	33
Figure 22: Adsorption and desorption isotherms of poly(DEB)-P-2 and its precursor	34
Figure 23: BET isotherm of the sample Poly(DEB)-Sim	35
Figure 24: Possible structures prepared by the Sonogashira reaction proceeding simultaneously with the polymerization.	35
Figure 25: NMR spectra of Poly(DEB)-P-2 and Poly(DEB)-Sim	36
Figure 26: BET isotherms of Poly(DEF), Poly(DET)-C and Poly(DET)-T	39
Figure 27: Reaction scheme of DEF polymerization	40
Figure 28: scheme of DET polymerization	41
Figure 29: difference in colour between Poly(DEB) and Poly(DET)	42

LIST OF TABLES

Tab. 1: microporous materials divided by size of pores	15
Table 2: Compositions of prepared polymers, BET surface area, pore volume and nitrogen content in samples modified with.....	37

LIST OF SUPPLEMENTARY DATA

Supplementary data A: NMR spectras of protected and de-protected monomers prepared in laboratory	44
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