AMINE-FUNCTIONALIZED POROUS POLYMERS FOR SELECTIVE CO_2 ADSORPTION

Kateřina SETNIČKOVÁ, Karel JEŘÁBEK, Tomáš STRAŠÁK, Karel SOUKUP

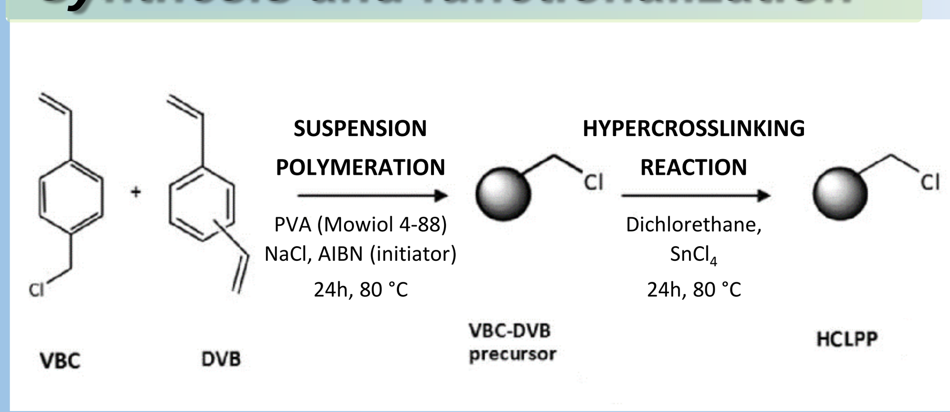
Institute of Chemical Process Fundamentals of the Czech Academy of Science, v.v.i.,
Department of Bioorganic Compounds and Nanocomposites, Rozvojová 2/135, CZ-165 02 Prague 6 – Suchdol, Czech Republic;
Tel.: +420220390268, e-mail: setnickova@icpf.cas.cz

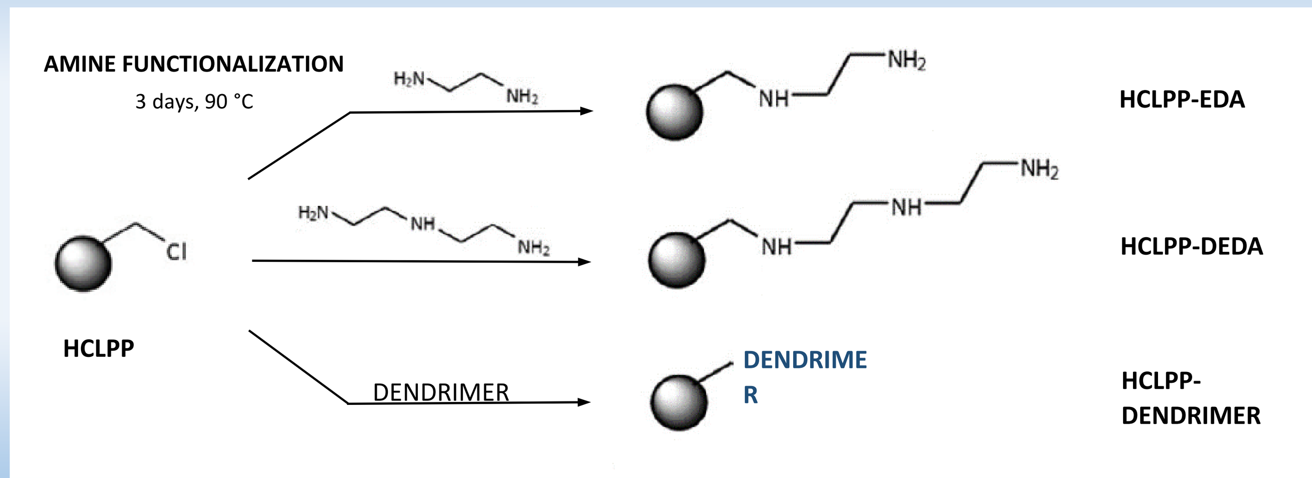
INTRODUCTION

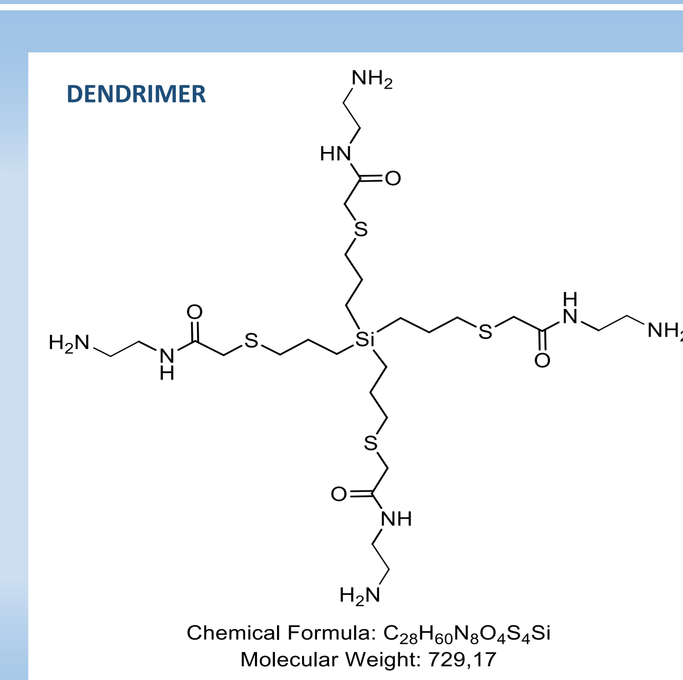
The increasing release of CO_2 to the atmosphere due to human activities has initiated considerable interest in the development of new materials and technologies for CO_2 capture. A cheap alternative solution represents a design and synthesis of microporous organic polymers, porous materials generally possess low skeletal density, in which the precise control over the material's chemical composition and textural properties can lead to a significant enhancement in gas storage [1]. This work is focused on the synthesis of hypercrosslinked vinylbenzyl chloride (VBC) - divinylbenzene (DVB) microporous material and its application for CO_2 capture and gas separation.

MATERIAL

Synthesis and functionalization







Scheme 1. Synthesis of hypercrosslinked porous polymer HCLPP (VBC-DVB) [2] and its amines functionalization HCLPP-EDA, HCLPP-DETA and HCLPP-DENDRIMER.

MATERIAL

Characterization

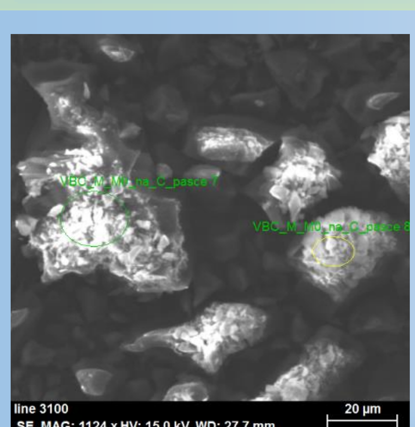


Figure 1 SEM analysis.

Table 1 Texture properties

Sample	S_{BET} ($m^2\,g^{-1}$)	S_{meso} ($m^2\,g^{-1}$)	V_{tot} ($mm^3_{liq}\,g^{-1}$)	V_{micro} ($mm^3_{liq}\,g^{-1}$)	ρ_{He} ($g\,cm^{-3}$)
HCLPP	757	310	408	226	1.15
HCLPP - EDA	283	93	157	97	1.18
HCLPP - DETA	277	132	159	76	1.16
HCLPP - DENDRIMER	616	194	341	218	1.69

S_{BET} specific surface area calculated by the BET method; S_{meso} specific surface area of mesopores (*t*-plot method);
V_{tot} specific total volume of pores; V_{micro} specific volume of micropores (*t*-plot method); ρ_{He} skeletal density (Helium pycnometry)

Table 2 EDX analysis

Sample	*C* (%)	*Cl* (%)	*N* (%)	*S* (%)	*Si* (%)
HCLPP	93.49	0.40	1.66	-	0.05
HCLPP - EDA	82.96	0.07	8.43	-	0.09
HCLPP - DETA	85.09	0.05	8.76	-	0.07
HCLPP - DENDRIMER	90.62	0.29	5.18	0.19	0.20

EXPERIMENTAL

Gas uptake calculation

The adsorption isotherms measurement was based on the volumetric method [2]. The gas amount adsorbed in the material is calculated from the balance as the difference of the initial and the equilibrium amounts:

$$N_{(adsorbed)} = N_{(gas\ initially)} - N_{(rest\ gas\ in\ equilibrium)} \quad (1)$$

$$N_{(adsorbed)} = \frac{p_1 V_1 - p_{eq}(V_1 + V_2 - V_x)}{RT} \quad (2)$$

The ideal gas state eq. (3) is used to the moles in gas phase calculation (*N* gas moles number):

$$N = \frac{pV}{RT} \quad (3)$$

The adsorbed amount is related to the material weight *m* to determine the adsorbed phase concentration, *q*:

$$q = \frac{N_{(adsorbed)}}{m} \quad (4)$$

Adsorption apparatus

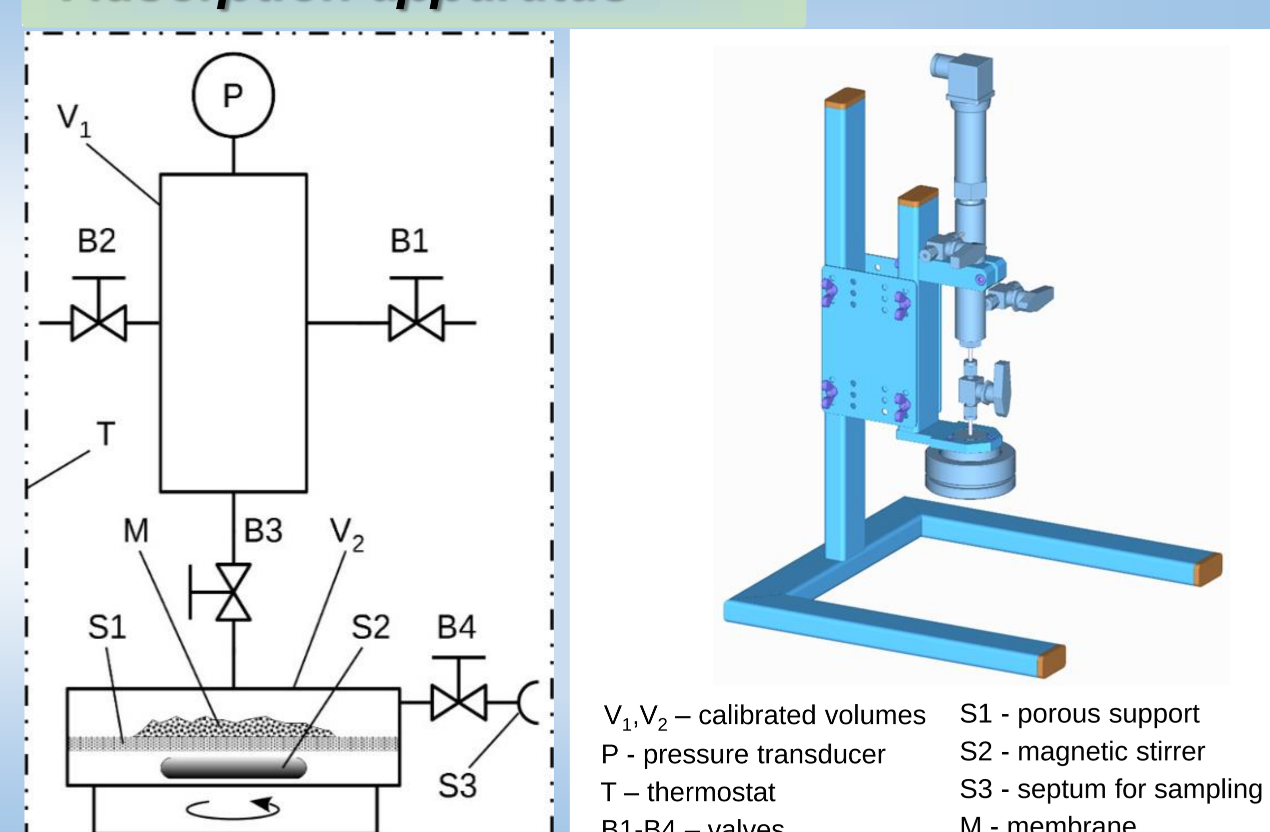


Figure 2 Apparatus for gas adsorption measurement in materials.

RESULTS

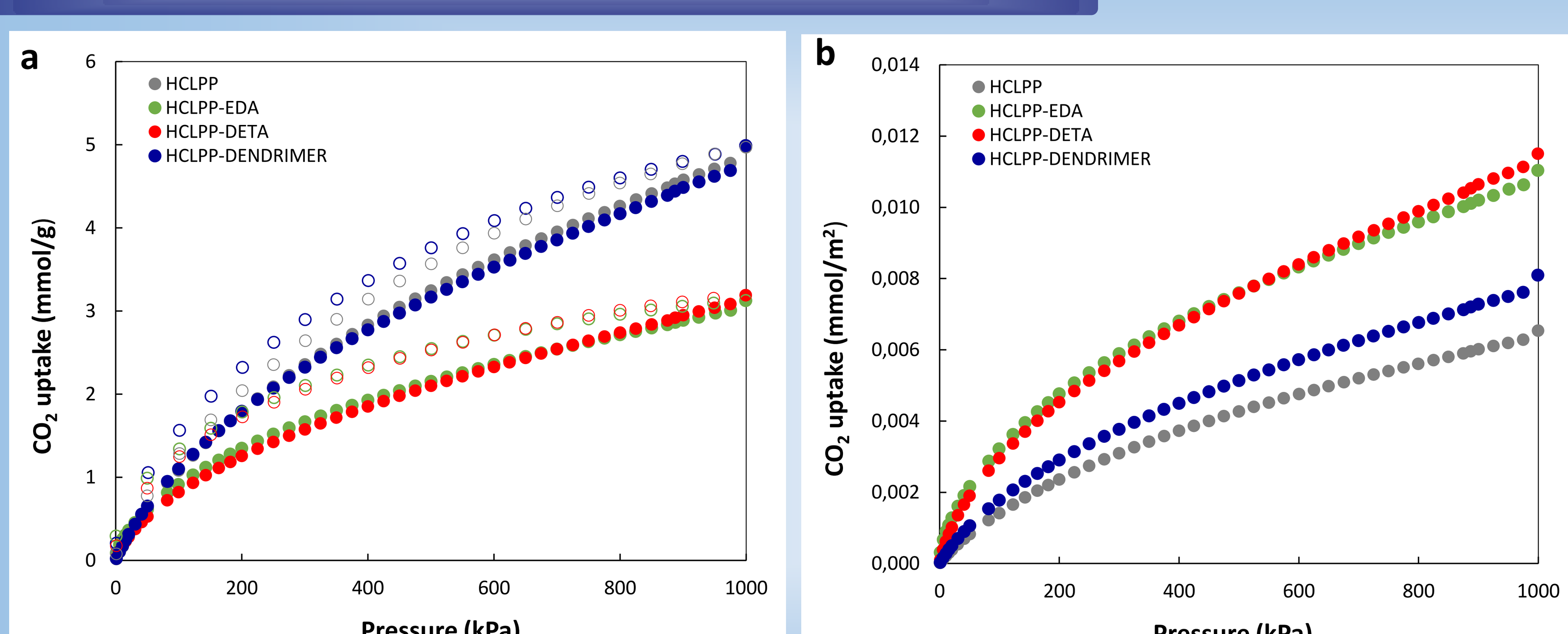


Figure 3 The CO_2 adsorption isotherms in the porous polymer materials at temperature 25 °C.
(a) adsorption (full points) and desorption (empty points),
(b) adsorption related to the specific surface area of porous polymers.

Table 3 Gas adsorption performance of materials

Sample	CO_2 ($mmol\,g^{-1}$)*	CH_4 ($mmol\,g^{-1}$)*	N_2 ($mmol\,g^{-1}$)*	H_2 ($mmol\,g^{-1}$)*	O_2 ($mmol\,g^{-1}$)*
HCLPP	1.01	0.31	0.090	0.021	0.012
HCLPP - EDA	0.82	0.13	0.029	0.015	0.047
HCLPP - DETA	0.91	0.13	0.033	0.012	0.042
HCLPP - DENDRIMER	1.10	0.24	0.063	0.017	0.089

***** *Amount of captured gases in porous material at 1 bar.*

Table 4 Selectivity performance of materials

Sample	CO_2/CH_4 (-)	CO_2/N_2 (-)	CO_2/H_2 (-)	O_2/N_2 (-)	CH_4/H_2 (-)
HCLPP	3.3	11.2	48.1	0.1	14.8
HCLPP - EDA	6.3	28.3	61.3	1.6	8.7
HCLPP - DETA	7.0	27.6	75.8	1.3	10.8
HCLPP - DENDRIMER	4.6	17.5	64.7	1.4	14.1

CONCLUSION

New porous polymeric sorbent with a high apparent surface area showing selective CO_2 adsorption over CH_4 and N_2 was prepared by suspension polymerization of vinylbenzyl chloride and divinylbenzene, followed by modification with polyamines and dendrimer containing amino groups resulting in an enhanced CO_2/CH_4, CO_2/N_2 and CO_2/H_2 selectivity. Produced polymer represents a promising organic porous material for CO_2 capture from gas mixtures. We plan to use the developed porous polymer and its amine-functionalized forms as fillers for preparation of mixed matrix membranes with improved CO_2/CH_4 and CO_2/N_2 separation performance.

ACKNOWLEDGEMENT

The financial support of the Czech Science Foundation (grant N° 19-23760J) and the ERDF/ESF project "UniQSurf-Centre of Biointerfaces and Hybrid Functional Materials" (no. CZ.02.1.01/0.0/0.0/17_048/0007411) is greatly appreciated.

REFERENCES

[1] YL. Luo, BE. Tan, Porous Materials for Carbon Dioxide Capture Book Series: Green Chemistry and Sustainable Technology (2014) 143-180.
[2] P. Veverka, K. Jeřábek, Mechanism of hypercrosslinking of chloromethylated styrene-divinylbenzene copolymers, Reactive & Functional Polymers 41 (1999) 21–25.