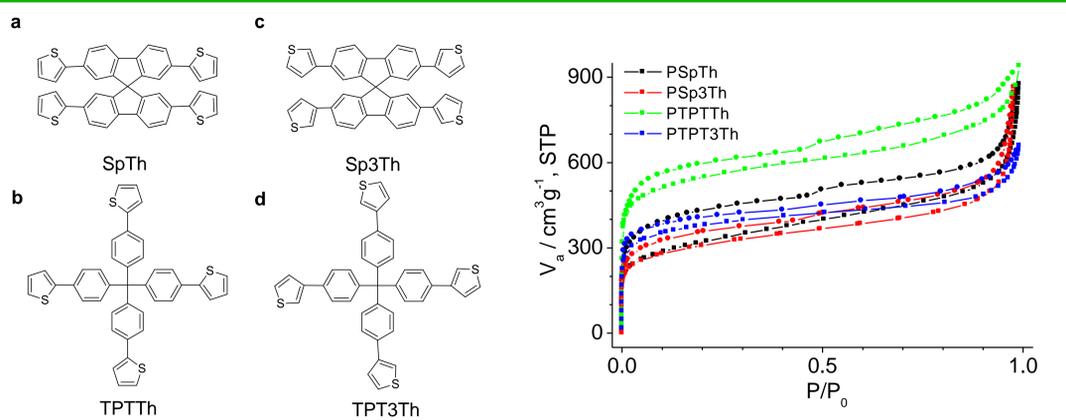


# Thiophene-based Microporous Polymer Networks via Chemical and Electrochemical Oxidative Polymerization

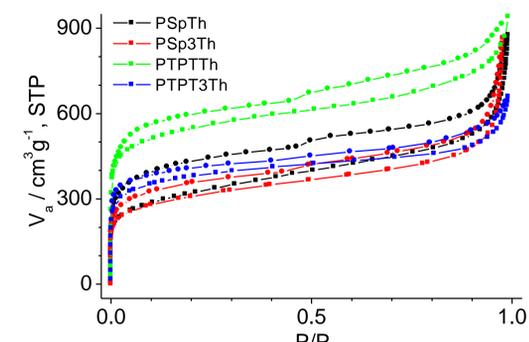
A. Palma-Cando<sup>a</sup>, G. Brunklaus<sup>b</sup>, U. Scherf<sup>a\*</sup>  
<sup>a</sup> Macromolecular Chemistry Group, Bergische Universität Wuppertal, Gaußstraße 20, D-42119 Wuppertal, Germany  
<sup>b</sup> Westfälische Wilhelms-Universität, Institut für Physikalische Chemie, Corrensstr. 46, D-48149 Münster, Germany.  
 \* scherf@uni-wuppertal.de

## Introduction

Microporous polymer networks (MPNs) have attracted enormous attention in the materials science community due to their promising properties: high surface area, well-distributed porosity, chemical and thermal resistance, among others. Hence, MPNs promise a high application potential in gas capture and separation, catalysis, organic electronic devices and sensors. Thiophene-based MPNs are especially interesting due to their possible applications in electronic devices. Nevertheless, these materials mainly have been obtained as insoluble powders. Processing MPNs into thin films or layers is a major challenge towards many practical applications. A way to overcome the processing problems is an electrochemical polymerization of multifunctional monomers on a suited substrate.[1] Mostly carbazole-based multifunctional monomers have been electropolymerized due to their low oxidation potential. We have recently reported a direct relation between the number of carbazole moieties in the monomer and the obtained specific surface area ( $S_{BET}$ ) of electrogenerated MPN films, as well as the use of the MPN films as electrochemical sensors for nitroaromatic analytes.[2] Moreover, it has been shown that the necessary electropolymerization potential of thiophenes can be strongly reduced by adding boron trifluoride diethyl etherate (BFEE) resulting in enhanced mechanical and electrical properties of the films.[3] In a recent study,[4] we reported the synthesis of four tetra-thienyl-substituted rigid monomers in Stille- or Suzuki-type coupling reactions. Microporous polymer networks were obtained as powders by oxidative polymerization of the monomers with iron trichloride showing  $S_{BET}$  of up to 2020  $m^2g^{-1}$  from nitrogen gas sorption measurements. Corresponding, electrochemically generated MPN films have been produced in boron trifluoride/dichloromethane mixtures showing  $S_{BET}$  values of up to 2135  $m^2g^{-1}$ , from the corresponding krypton gas sorption isotherms. The MPN films produced in presence of boron trifluoride exhibited higher specific surface areas and a more defined electrochemical behavior if compared to the corresponding networks made in absence of boron trifluoride probably due to the exclusive formation of bithiophene connections. Electrochemical reduction of 1,3,5-trinitrobenzene at glassy carbon electrodes modified with our thiophene-based MPNs clearly indicates a direct relationship between specific surface area and current response via an adsorption-controlled interaction of the electron-poor nitroaromatic compound and the electron-rich thiophene-based MPN.



**Scheme 1.** Chemical structures of the investigated thiophene-based monomers: a) SpTh, b) TPTTh, c) Sp3Th, and d) TPT3Th.

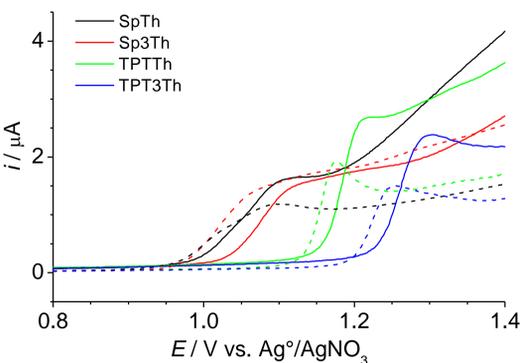


**Fig. 1.** Nitrogen gas sorption isotherms of chemically synthesized MPN bulk polymers (oxidation with  $FeCl_3$ ).

**Table 1.** Porosity data, gas uptake (at 298 K) and selectivity of chemically synthesized bulk MPNs.

Polymer	$S_{BET}$ [ $m^2g^{-1}$ ]	Pore volume <sup>a</sup> [ $cm^3g^{-1}$ ]	Gas uptake [%]			Selectivity <sup>c</sup>		
			$CO_2$	$N_2$	$CH_4$	$H_2$ <sup>b</sup>	$CO_2/N_2$	$CO_2/CH_4$
PSpTh	1153	0.90	7.19	0.38	0.92	1.38	12.1	2.8
PSp3Th	1102	0.85	6.88	0.38	0.95	1.37	11.5	2.6
PTPTTh	2020	1.22	7.61	0.73	1.15	1.81	6.6	2.4
PTPT3Th	1390	0.82	7.88	0.48	1.10	1.67	10.5	2.6

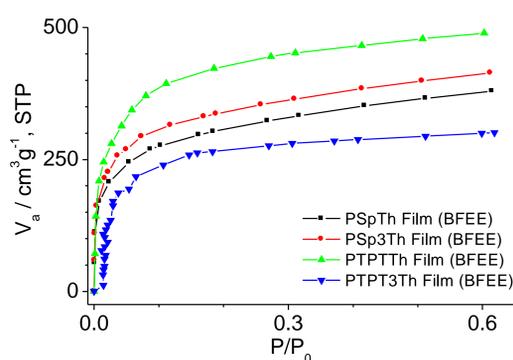
<sup>a</sup> Determined at  $P/P_0 = 0.95$ , <sup>b</sup> Measured at 77 K, <sup>c</sup> Calculated by applying Henry's law



**Fig. 2.** First anodic scan voltammograms for 0.1 mM solutions of the monomers and 0.1 M tetrabutylammonium tetrafluoroborate in DCM (solid lines) and BFEE/DCM (1:4) (dashed lines) at Pt disc electrodes, the voltammograms were recorded from 0 to 1.4 V with a scan rate of 0.10  $Vs^{-1}$ .

**Table 2.** Onset potential for electrochemical polymerization of thiophene-based monomers in dichloromethane and BFEE/DCM (1:4) solutions.

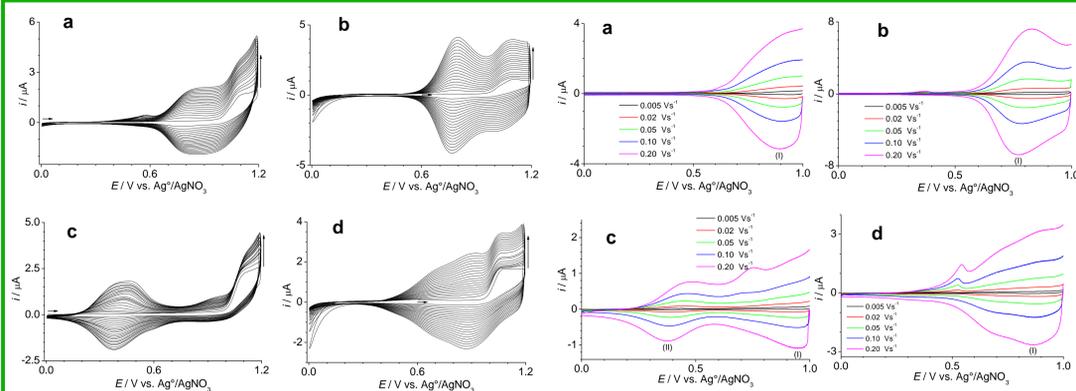
Monomer	$E_{onset}$ [V] vs $Ag^+/AgNO_3$		$\Delta E$ [mV]
	DCM	BFEE/DCM	
SpTh	0.99	0.96	30
Sp3Th	1.04	0.98	60
TPTTh	1.16	1.11	50
TPT3Th	1.23	1.20	30



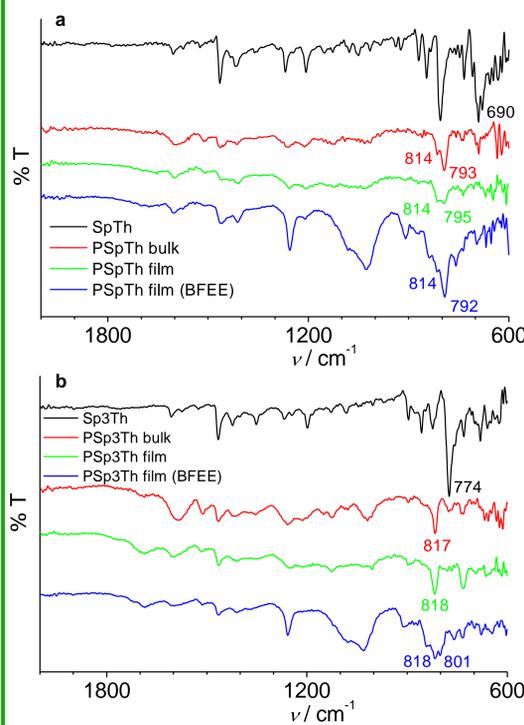
**Fig. 3.** Kr gas adsorption isotherms of electropolymerized MPN films prepared in BFEE/DCM (1:4).

**Table 3.** Specific surface areas of electropolymerized MPN films, prepared in DCM and BFEE/DCM (1:4) by using Kr gas sorption. All  $S_{BET}$  film measurements were carried out 4 times.

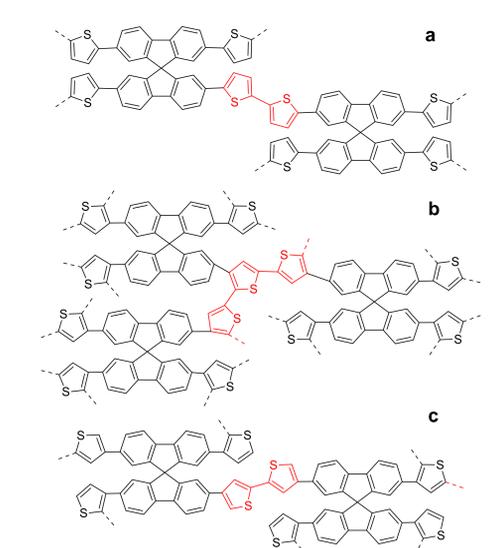
MPN films	$S_{BET}$ [ $m^2g^{-1}$ ]	
	DCM	BFEE/DCM
PSpTh	815 ± 115	1240 ± 84
PSp3Th	1099 ± 176	1576 ± 27
PTPTTh	1258 ± 52	2135 ± 147
PTPT3Th	927 ± 217	1114 ± 197



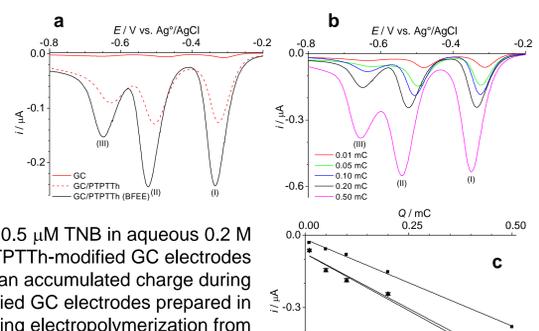
**Fig. 4.** Twenty consecutive cyclic voltammograms during electropolymerization of (a, b) SpTh, and (c, d) Sp3Th; potential range: 0 to 1.2 V, scan rate: 0.10  $Vs^{-1}$ , at Pt disc electrodes, 0.1 mM monomer solutions in DCM (a,c) BFEE/DCM (1:4) (b,d), 0.1 M TBABF<sub>4</sub> as supporting electrolyte.



**Fig. 6.** FT-IR spectra of monomers: (a) SpTh and (b) Sp3Th (black lines); the resulting bulk polymers (red lines); the resulting MPN films prepared by electropolymerization in pure DCM (green lines); and the resulting MPN films prepared by electropolymerization in BFEE/DCM (1:4) (blue lines).



**Scheme 2.** Idealized chemical structures of MPN films (a) PSpTh, (b) PSp3Th prepared in DCM, and (c) PSp3Th prepared in BFEE/DCM (1:4).



**Fig. 7.** Linear scan voltammograms (LSV) for the reduction of 0.5  $\mu M$  TNB in aqueous 0.2 M KCl and 0.1 M PBS solution (a) at non-modified, and PTPTTh-modified GC electrodes prepared in DCM and BFEE/DCM (1:4) solutions for an accumulated charge during electropolymerization of 0.20 mC, (b) PTPTTh-modified GC electrodes prepared in BFEE/DCM (1:4) solution for an accumulated charge during electropolymerization from 0.01 to 0.50 mC, and (c) plot of peak current versus accumulated charge during electropolymerization under formation of PTPTTh-modified GC electrodes in BFEE/DCM (1:4) solution. LSVs were obtained with a scan rate of 0.01  $Vs^{-1}$ .

## Conclusions

- A series of tetrafunctional thiophene-based monomers was chemically and electrochemically polymerized resulting in microporous polymer networks with high specific surface areas of up to 2135  $m^2g^{-1}$  for thin films and 2020  $m^2g^{-1}$  for powdery bulk materials.
- Electrochemical polymerization in dichloromethane (DCM)/boron trifluoride diethyletherate (BFEE) mixtures generally produced MPN films with higher surface area and a more defined electrochemical behavior if compared to ones made in pure DCM.
- Different coupling patterns have been observed for 3-thienyl-substituted monomers in the presence or absence of boron trifluoride as additive: In the presence of BFEE the preferred formation of bithiophene bridges was observed, thus enhancing the microporosity of the materials.
- The aqueous electrochemical reduction of TNB at non-modified and PTPTTh-modified GC electrodes showed a much increased cathodic current response for the modified electrodes, most probably driven by interactions of electron-poor nitroaromatic analyte molecules and the electron-rich thiophene-based MPN films with their high surface area

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