

# Surface-Initiated Synthesis of Conjugated Microporous Polymers: Chain-Growth Kumada Catalyst-Transfer Polycondensation at Work

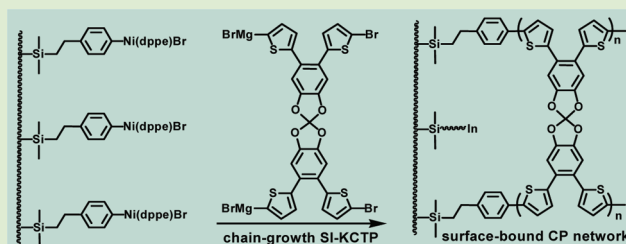
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## S Supporting Information

**ABSTRACT:** Most of conjugated microporous polymers (CMPs) prepared to date are poorly processable, intractable solids. The immobilization of CMPs onto various surfaces is strongly desirable for many applications, such as for gas storage and separation, heterogeneous catalysis, and so forth. However, the preparation of thin porous films remains a challenging task. This Letter reports Ni-catalyzed surface-initiated Kumada catalyst-transfer polycondensation of a tetrafunctional thiophene-based (AB) 2-monomer from organosilica microparticles leading to microparticles covered by thin-film ( $\sim 30$  nm) layers of the CMP. A sample of unbound CMP was also prepared by a bulk polymerization of the same monomer. Thus-obtained CMP possesses a relatively high specific surface area of  $463 \text{ m}^2 \text{ g}^{-1}$ . The porosity of the immobilized polymer is somewhat lower with a specific surface area of  $123 \text{ m}^2 \text{ g}^{-1}$ .



Novel porous materials, such as metal–organic frameworks (MOFs), porous polymers (PIMs, EOFs, HCPs, etc.), or carbide-derived carbons (CDCs) attract increasing attention due to their potential applications in adsorption, separation, biomedical devices, and heterogeneous catalysis.<sup>1</sup> Conjugated microporous polymers (CMPs)<sup>2</sup> is another promising class of porous materials which, in addition to the above-mentioned applications, are potentially useful in organic electronics. It is because of a  $\pi$ -conjugated nature of the frameworks, optical and electronic properties of which can be finely modulated by adsorption of various guests such as chromophores, hole, or electron conductors.<sup>3</sup> CMPs can be obtained via different reaction routes employing C–C coupling reactions, similar to the coupling polycondensations developed for the preparation of conventional, linear conjugated polymers.<sup>4–8</sup> Thus, Gilsh,<sup>4</sup> Sonogashira-Hagihara,<sup>5</sup> Suzuki,<sup>6</sup> and Yamamoto<sup>7</sup> couplings as well as oxidative polymerizations<sup>8</sup> have been already employed to synthesize a variety of microporous networks, such as spirobifluorene-, thiophene-, and arylene-ethynylene-based ones. However, most of the CMPs prepared in such a way are intractable solids. The interest to porous materials would be considerably increased if they could be processed as thin homogeneous films immobilized onto either planar supports or micro/nanoparticles. Although several approaches were reported for the processing of MOFs into thin films,<sup>9,10</sup> methods for the preparation of CMP thin films still need to be developed.

Surface-initiated polymerization (SIP), the method of growing polymers selectively from functionalized surfaces or particles by a chain-growth polyaddition of monomers to surface-immobilized initiators, is one of the most powerful and fast methods for the controlled preparation of covalently

grafted thin polymer films.<sup>11</sup> However, because of a step-growth character of most of the AA+BB condensation polymerization routes employed for preparation of conjugated polymers, the SIP approach has never been successfully applied for the grafting of CMPs from surfaces. Nowadays, the preparation of many complex topologies of conjugated polymers became feasible owing to chain-growth polycondensations of AB-type monomers discovered by McCullough et al.<sup>12</sup> and Yokozawa et al.<sup>13</sup> and further developed by others.<sup>14</sup> Very recently, we introduced surface-initiated Suzuki<sup>15</sup> and Kumada<sup>16</sup> catalyst-transfer polycondensation (SI-KCTP) of AB-type monomers leading to conjugated polymer brushes,<sup>16</sup> developed on planar surfaces as well as on micro- and nanoparticles.<sup>17</sup>

This Letter reports the first, to the best of our knowledge, example of SI-KCTP of tetrafunctional (AB) 2-monomers leading to the formation of thin films of CMPs attached to micrometer organosilica particles. According to our method, the Ni initiator was covalently immobilized onto organosilica microparticles, and then the (AB) 2-monomer was added. An important feature of the developed process is that the polymerization of the monomer proceeded only from the surface but not in the bulk solution so that the formation of unbound CMP was eliminated.

Scheme 1 shows the synthetic route to a monomer precursor, tetrabromide **1**, containing a pair of  $\pi$ -conjugated subunits each comprising two bromothiophene and one phenyl rings linked by a nonconjugated spiro-orthocarbonate bridge. The synthesis

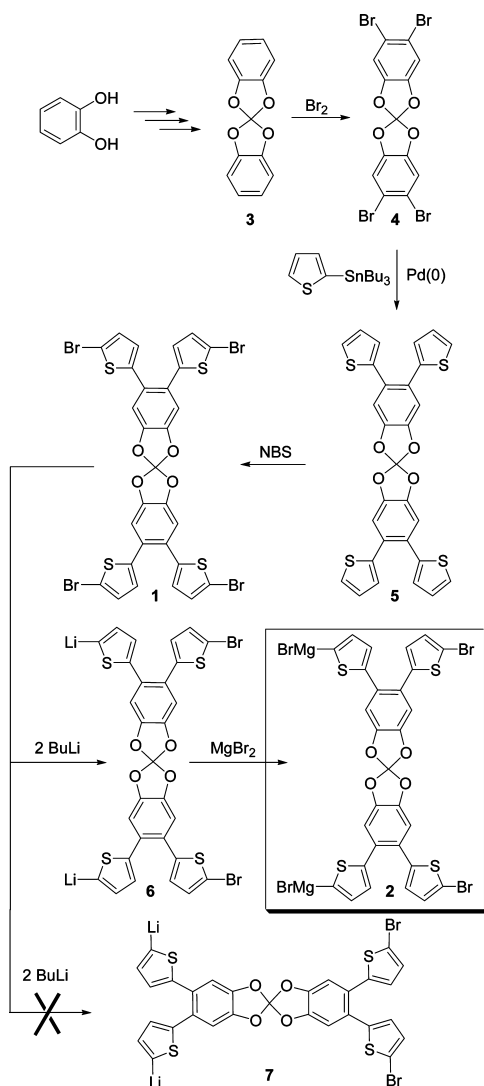
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Scheme 1. Synthesis of the Monomer



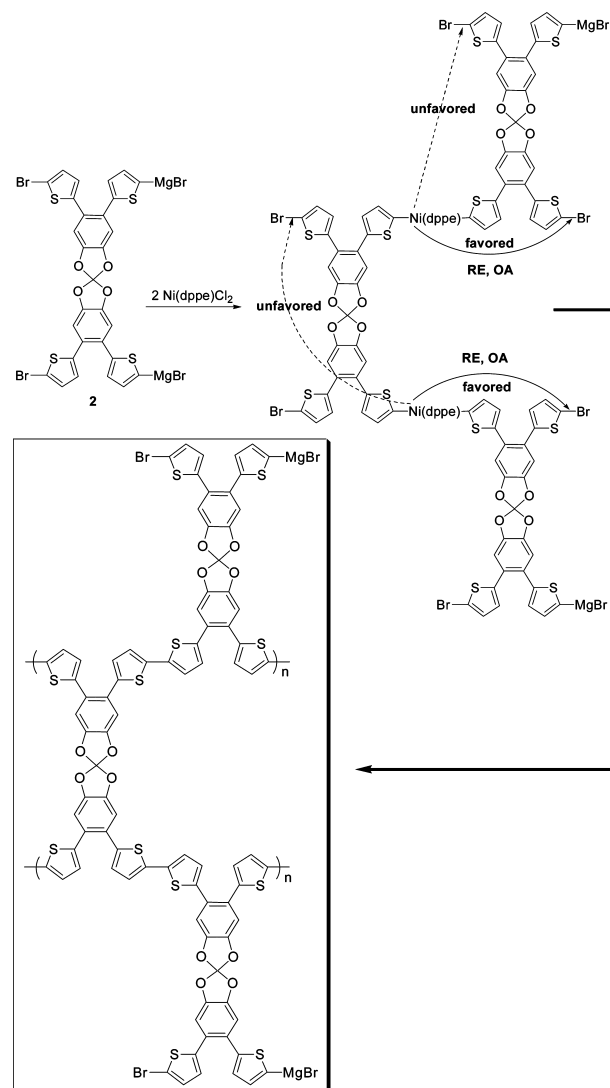
of the monomer **2** was accomplished by the treatment of **1** with 2 equiv of BuLi at  $-78\text{ }^{\circ}\text{C}$  followed by the addition of  $\text{MgBr}_2$ .  $^1\text{H}$  NMR spectroscopy reveals a high selectivity of the dilithiation process leading to the introduction of only one lithium into each  $\pi$ -conjugated subunit (Scheme 1). We suggest that the first lithiation makes this particular subunit less reactive toward BuLi (because of increased electron density); therefore the second lithium is introduced predominantly into another subunit (Figure S1, Supporting Information).

An essential feature of the synthetic approach developed herein is the use of the (AB) **2**-monomer, that is, the monomer which consists of two  $\pi$ -conjugated subunits, and each subunit acts as a AB-monomer (A and B here are self-reactive under Kumada coupling conditions C–MgBr and C–Br groups, respectively). According to our idea, the (AB) **2**-structure of the monomer **2** must ensure that, under KCTP conditions, each AB-subunit will be independently polymerized on the chain-growth manner leading to the conjugated polymer network. This polymerization process is similar to the chain-growth polymerization of other AB-monomers into linear conjugated polymers under KCTP conditions. However, the presence of the spiro-ortho-carbonate bridge in the monomer structure will

ensure the formation of cross-linking points between conjugated polymer strands at every repeat unit.

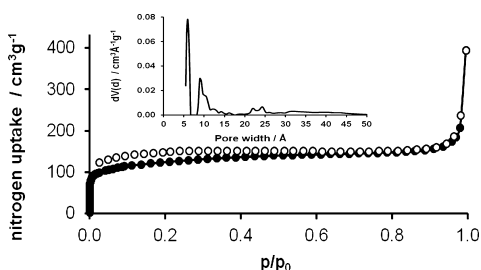
In KCTP, the chain growth occurs via iterative transmetalation (TM), reductive elimination (RE), and oxidative addition (OA) steps, whereby nickel is not released from the chain. The chain-growth mechanism results from the fact that, within each chain-propagation cycle, the Ni(0) catalytic species eliminated upon the RE step do not dissociate from the chain and do not react with other monomer molecules or other halides but instead undergo intramolecular OA into the C–Br bond present in the same chain. Ni(0) during the polymerization undergoes a ring-walking process along  $\pi$ -conjugated systems.<sup>14f</sup> It was also demonstrated that, if the Ni catalyst is properly immobilized on the surface, the polymerization occurs selectively from the surface, and not in the bulk solution, thus resulting into surface-tethered polymer chains (polymer brushes).<sup>16</sup> We assumed that the  $\pi$ -conjugated nature of the subunits in the monomer **2** would facilitate the intramolecular catalyst ring-walking process preventing diffusion of the Ni catalysts into the bulk solution (which corresponds the step-growth polymerization of **2** and results into a bulk network, see Scheme 2).<sup>18</sup>

Scheme 2. Preparation of the Network CMP-2



To estimate a general feasibility of the KCTP method for the preparation of CMPs, a bulk polymerization of the monomer **2** in the presence of Ni(dppe)Cl<sub>2</sub> was investigated first. It was found that the addition of the catalyst to the solution of the monomer **2** in tetrahydrofuran (THF) at room temperature resulted into a rapid precipitation of the reaction product, further designated as CMP-2. It was washed, subjected to Soxhlet extraction with various solvents, and dried in vacuum. Elemental analysis reveals the presence of Br in the product in a quantity corresponding to about 91% conversion of reactive groups in the monomer **2** (section 5 of Supporting Information). Thermogravimetric analysis (TGA) shows that the decomposition of CMP-2 occurs in 450–600 °C temperature range (maximum at 530 °C), which is typical behavior for thiophene-based conjugated polymers and corresponding networks (Figure S2).

To estimate the porosity of CMP-2 the physisorption experiments involving different probe gases, namely, nitrogen (at 77 K), hydrogen (77 K), methane (298 K), and water (at 298 K) were performed. The nitrogen physisorption isotherm exhibits type-I behavior according to the International Union of Pure and Applied Chemistry (IUPAC) classification, which is typical for microporous materials (Figure 1). The hysteresis



**Figure 1.** Nitrogen adsorption (solid symbols) and desorption (empty symbols) isotherms of CMP-2 at 77K. Inset: Differential pore size distribution curves obtained by applying QSDFT on the adsorption isotherm.

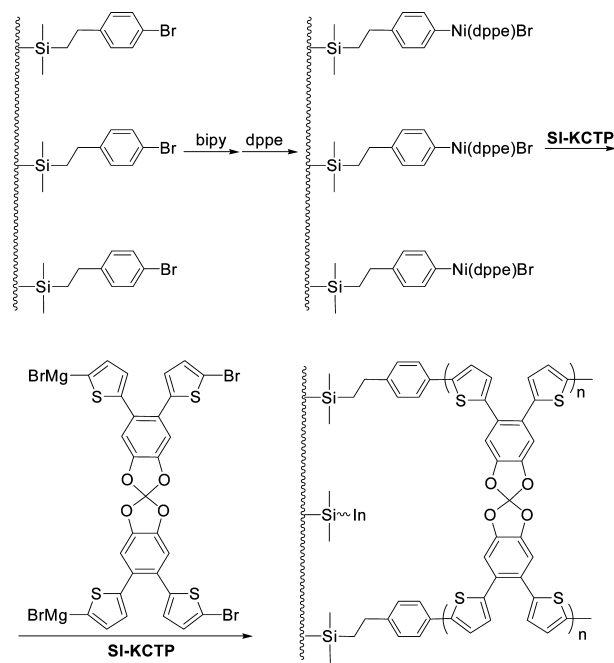
observed is caused by pore swelling of the polymers during the measurement. The specific surface area derived from the adsorption branch using the multipoint BET model amounts to 463 m<sup>2</sup> g<sup>-1</sup>, and the micropore volume is 0.27 cm<sup>3</sup> g<sup>-1</sup> (at  $p/p_0 = 0.90$ ). Figure 1 (inset) displays the results of pore size analysis by applying the quenched solid density functional theory (QSDFT) method, assuming slit and cylindrical pore geometry. The two main peaks, corresponding to the pores with diameters of 5.9 Å and 9.2 Å, are observed.

The maximum hydrogen and methane excess uptake is 1.1 wt % (at 77 K) and 52 mg g<sup>-1</sup> (at 298 K), respectively (Figures S3 and S4, Supporting Information). The adsorption of water at 298 K (Figure S5) takes place only at very high relative pressures, which is indicative of a highly hydrophobic material. The total pore volume calculated from water adsorption isotherm (at  $p/p_0 = 0.97$ ) amounts to only 0.06 cm<sup>3</sup> g<sup>-1</sup>.

In the next step, the SIP of **2** from microparticles was studied. Monodisperse, 880 nm in diameter, silica particles having 10 nm thick organosilica shells were prepared by a modified Stöber method via sequential solgel hydrolysis of tetramethyl orthosilicates (TMOS) and [2-(4-bromo-phenyl)-ethyl]-triethoxy-silane.<sup>17</sup> The latter silane provides a useful functionality on the surface of the particles, required for catalyst immobilization. Initiating sites were developed by the treatment

of the particles consecutively by Et<sub>2</sub>Ni(bipy) and dppe (Scheme 3). Because the initiator was immobilized to the

### Scheme 3. Surface-Initiated Polymerization of **2**: Preparation of Microparticles Having a Microporous Conjugated Polymer Shell

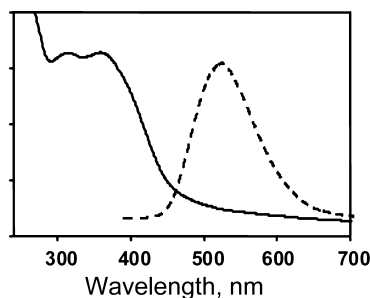


microparticles via a flexible Si-(CH<sub>2</sub>)<sub>2</sub>-Ph-linkage, monomer molecules have a possibility for attaching to the microparticles using both Grignard functions. Prior to the SI-KCTP, the particles were carefully purified from physisorbed Ni compounds by several centrifugation/redispersion cycles utilizing anhydrous and degassed THF in an argon atmosphere. To perform SI-KCTP, monomer **2** was added to the dispersion of the activated particles, and the polymerization was performed at room temperature for 40 min. Afterward, the resulting composite particles were carefully separated from any ungrafted materials. According to TGA, the resulting particles having CMP-2 shells (further designated as  $\mu$ -CMP-2 particles) lost ~15% of their weight in the temperature interval from 450 to 600 °C in an oxygen atmosphere which is a typical decomposition behavior of CMP-2 (Figure S6, Supporting Information). For the given particle size and densities of the components, the CMP-2 content in the  $\mu$ -CMP-2 particles correspond to the thickness of the CMP-2 shell ~30 nm. SEM measurements reveal that SI-KCTP induces a significant increase of the particle surface roughness and increase of their diameter from 880 nm for unmodified particles up to 940 nm for the  $\mu$ -CMP-2 particles that corroborates the shell thickness of ~30 nm (Figure S7).

The porosity of the composite particles was proven by nitrogen physisorption at 77 K. The steep increase of the adsorbed amount in the low relative pressure region points to the presence of microporosity. Also the shape of the isotherm (hysteresis) is indicative for adsorption on a flexible system,<sup>19</sup> confirming the porosity of the grafted film (Figure S8 of the Supporting Information). The specific surface area calculated for grafted polymer after exclusion of the mass of silica support amounts to 123 m<sup>2</sup> g<sup>-1</sup> which is lower in comparison to the bulk polymer. The lowered porosity for the grafted films may

be explained by a lowered rigidity of two-dimensional (2D) networks (thin films) compared to their three-dimensional (3D) counterparts (bulk). Indeed, 2D networks have generally a larger number of unreacted functional groups at the network periphery; they are less strongly cross-linked and, hence, more prone to collapse upon drying than 3D networks. It is noteworthy that previously reported microporous polymer networks based on hyperbranched polyarylates, also displayed a modest specific surface area of  $158 \text{ m}^2 \text{ g}^{-1}$ .<sup>20</sup> Thus, the preparation of thin-film microporous polymers with very high microporosities remains a challenging task.

UV-vis absorption and fluorescence spectra of the  $\mu$ -CMP-2 particles dispersed in  $\text{CHCl}_3$  are very similar to the spectra of CMP-2 bulk (Figure S9, Supporting Information) which further confirm a successful grafting of the shell (Figure 2).



**Figure 2.** UV-vis absorption and emission spectra (solid and dashed lines, respectively) of the  $\mu$ -CMP-2 particles dispersed in  $\text{CHCl}_3$ .

A control experiment was performed which revealed that immobilization of the Ni initiator, as described above, was essential for the successful grafting of CMP-2 from the particles. Since we aimed to maximize the amount of the grafted CMP-2, the monomer was used in a large excess relative to the surface-bound initiator. Such conditions also favor the formation of unbound CMP-2 because the catalytic species dissociating from the growing surface-bound chains upon the chain termination can, in principle, initiate the polymerization of the excess monomer in the bulk solution. However, no free CMP-2 was formed in this experiment, and the excess monomer was recovered in its protonated form. The observed coexistence of polymerization product ( $\mu$ -CMP-2 particles) and unreacted monomer is a sign of the clean chain-growth polymerization behavior which is typical for KCTP of thiophene-based AB-monomers.<sup>12–14,16–18</sup>

In conclusion, Ni-catalyzed chain-growth Kumada catalyst-transfer polycondensation of the tetrafunctional (AB) 2-monomer was employed in the preparation of the thiophene-based conjugated microporous polymer. The resulting CMP-2 possesses a relatively high specific surface area of  $463 \text{ m}^2 \text{ g}^{-1}$ . Furthermore, surface-initiated KCTP was performed from properly functionalized organosilica microparticles which led to microparticles covered by a thin shell ( $\sim 30 \text{ nm}$ ) of the CMP. The porosity of the immobilized polymer is somewhat lower with a specific surface area of  $123 \text{ m}^2 \text{ g}^{-1}$  which is lower compared to the bulk polymer. Thus, the preparation of thin-film microporous polymers with very high microporosities remains a challenging task. Nevertheless, we believe that the developed surface-initiated polymerization route for the preparation of surface-bound thin-film conjugated polymer networks may be of interest for many applications ranging from gas sorption and separation to heterogeneous catalysis and

organic electronics. We envisage that such thin-film CMPs may be especially useful in cases when relatively expensive porous materials are utilized, and when only outmost layer of the porous material can be used efficiently because of diffusion limitations.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Description of instrumentation and materials used; experimental details for preparation of the monomer and polymerization procedure, SEM,  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  physisorption isotherms, and TGA data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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