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Two Novel Synthetic Approaches towards <u>Microporous Polymer Networks</u> C. Widling¹, E. Preis¹, R.S. Sprick¹ U. Scherf¹, J. Schmidt², A. Thomas²



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Introduction:

Two novel series of microporous polymer networks (MPNs) have been synthesized by acid catalyzed Friedel-Crafts-type self-condensation of A_2B_2 and A_2B_4 type fluorenone-based monomers (with e.g. 2,7-bis(*N*,*N*-diphenylamino) **A** or 2,7-bis[4-(*N*,*N*-diphenylamino)phenyl] **B** substitution (Figure 1)) and Lewis-acidic (TiCl₄) or acidic (MSA) cyclotrimerization of bifunctional diketo-*s*-indacene-type monomers. One synthetic challenge is to generate the MPNs straightforward under mild reaction conditions including moderate processing temperatures^[1] and without the use of transition metal catalysts.^[2]









Figure 2: Chemical structures of the monomers E-G

Figure 5: Idealized structure of the MPNs from monomers **E** (R = H) and **F** (R = methyl) (Reaction conditions: TiCl4, 1,2-dichlorobenzene, 180 °C, 72 h)

Figure 3: Idealized structure of the MPN from monomer **A** (R = phenyl) (Reaction conditions: MSA, 1,2-dichlorobenzene, 140 °C)



Figure 4: Idealized structure of the MPNs from monomer **G** (Reaction conditions: MSA, 1,2-dichlorobenzene, 180 °C, 3h)

Monomer(s)	S _{BET} m ² g ⁻¹	S _{BET} after CO ₂ washing m ² g ⁻¹	Total pore volume cm ³ g ⁻¹ [after CO ₂ washing]
Α	1420	1243	1.31 [0.90]
В	1161	1394	0.80 [0.85]
С	17	-	0.02
D	163	-	0.30
C/D (1:1)	947	1447	0.67 [0.97]
A/B (3:1)	1081	1103	*
A/B (1:1)	968	1748	0.77 [1.60]
A/B (1:3)	1221	1408	*
E	1165	-	*
F	395	-	*
G	1650	-	*
Not determined			

Table 1: Characterization data for the MPNs of this study







Figure 6: Nitrogen physisorbtion isotherm of the condensation products of monomers **A/B** (top) and **C/D** (bottom) **Figure 7**: Nitrogen physisorbtion isotherm of the condensation products of monomers **E** (top) **F** (middle) and **G** (bottom)

Conclusion: In summary, A_2B_4 -type monomers with 2,7-bis(*N*,*N*-diphenylamino) **A** or 2,7-bis[4-(*N*,*N*-diphenylamino)phenyl] **B** substitution of the fluorenone cores quantitatively form MPNs with high S_{BET} surface areas of up to 1400 m²g⁻¹ in a simple Friedel-Crafts-type self-condensation. 2,7-Disubstitution with *N*-phenyl-*N*-methylamino groups as well as 3,6-disubstitution give rise to drastically reduced S_{BET} values except for the mixture of the two extended monomers **C** and **D**. Supercritical CO₂ treatment can distinctly increase the porosity of the samples especially for MPNs made of binary monomer mixtures containing **A** and **B**. The supercritical CO₂ treatment seems to stabilize an expanded pore structure corresponding to the swollen state of the polymer network. The acid-catalyzed cyclotrimerization of bifunctional *s*-indacene-type monomers leads to a novel class of microporous ladder polymers with high surface areas up to 1650 m² g⁻¹.

References: [1] R. S. Sprick, A. Thomas, U. Scherf, *Polym. Chem.* 2010, **1**, 283. [2] E. Preis, C. Widling, U. Scherf, S. Patil, G. Brunklaus, J. Schmidt, A. Thomas, *Polym. Chem.* 2011, **2**, 2186.