

Two Novel Synthetic Approaches towards Microporous Polymer Networks

C. Widling¹, E. Preis¹, R.S. Sprick¹ U. Scherf¹, J. Schmidt², A. Thomas²

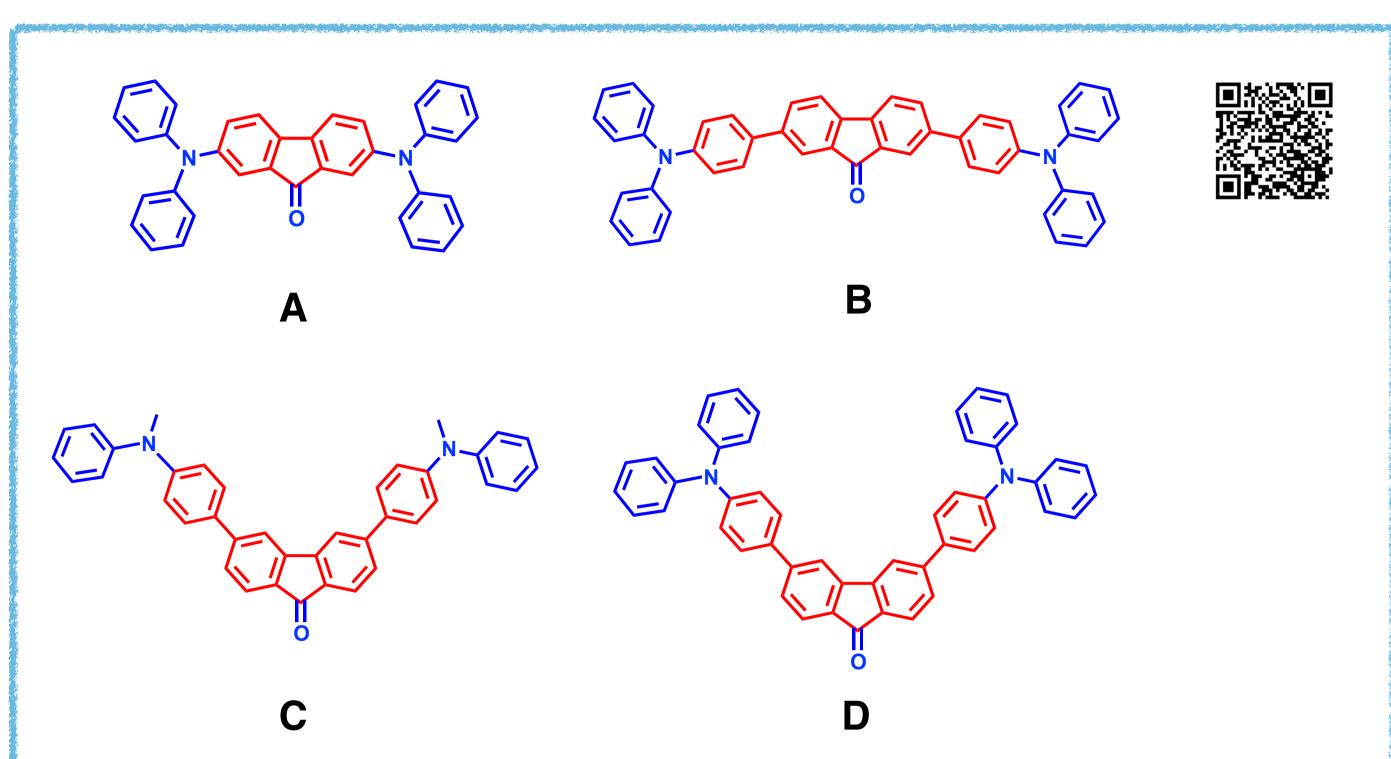
¹Bergische Universität Wuppertal, Makromolekulare Chemie und Institut für Polymertechnologie, Gaußstr. 20 D-42119 Wuppertal, Germany

²Institut für Chemie, Technische Universität Berlin, Englische Straße 20 D-10587 Berlin, Germany



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]



E F G

Figure 2: Chemical structures of the monomers E-G

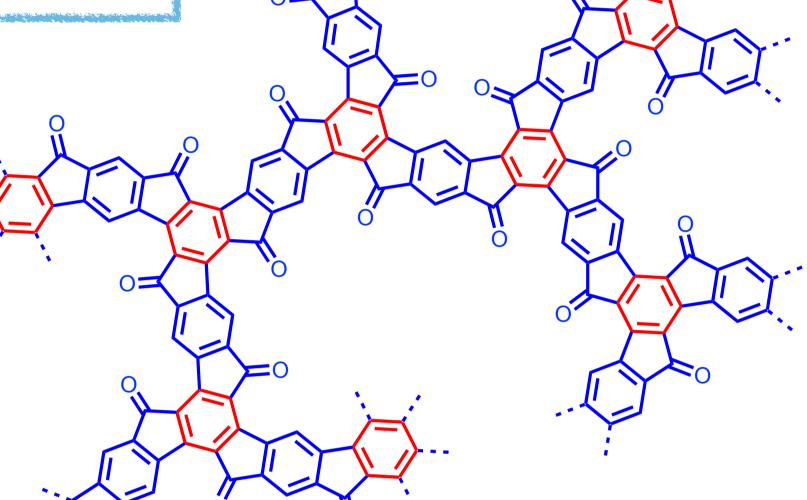


Figure 5: Idealized structure of the MPNs from monomers **E** (R = H) and **F** (R = methyl) (Reaction conditions: TiCl4, 1,2-dichlorobenzene, 180 °C, 72 h)

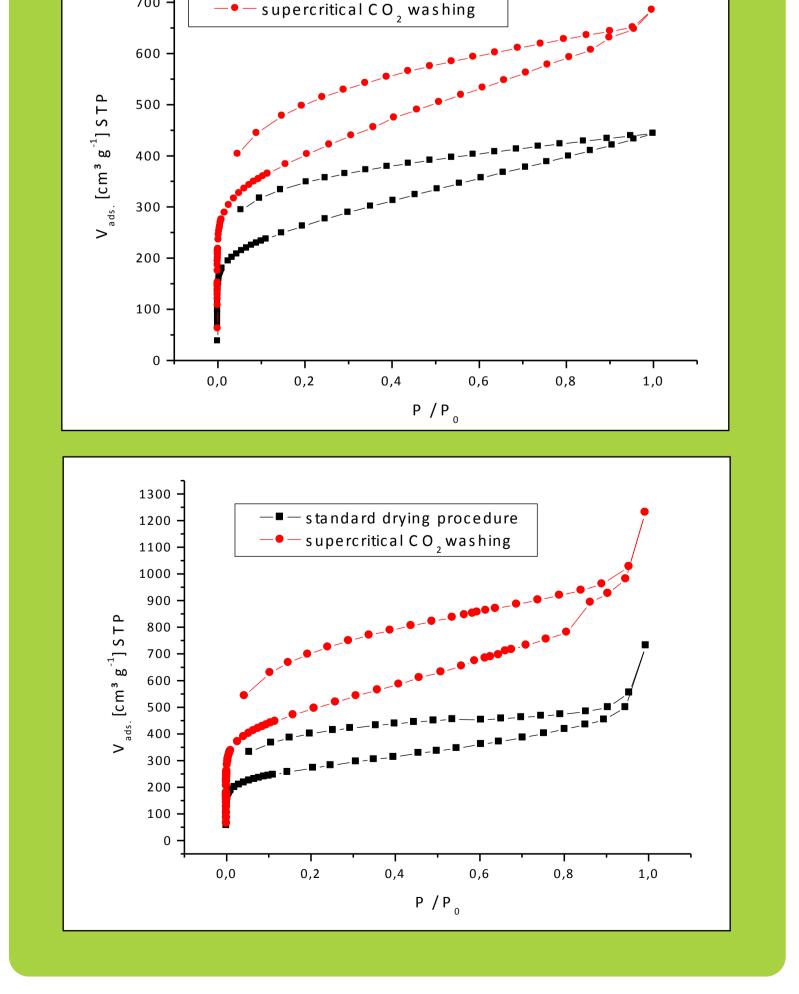
Figure 1: Chemical structures of the monomers A-D

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

Monomer(s) S_{BET} m²g⁻¹ **S**BET after **Total pore** CO₂ washing volume cm³g⁻¹ m²g⁻¹ [after CO₂ washing] 1420 1243 1.31 [0.90] 1394 0.80 [0.85] 1161 17 0.02 163 0.30 **C/D** (1:1) 947 1447 0.67 [0.97] **A/B** (3:1) 1103 1081 **A/B** (1:1) 1748 968 0.77 [1.60] **A/B** (1:3) 1221 1408 1165 395 1650 *Not determined

Table 1: Characterization data for the MPNs of this study

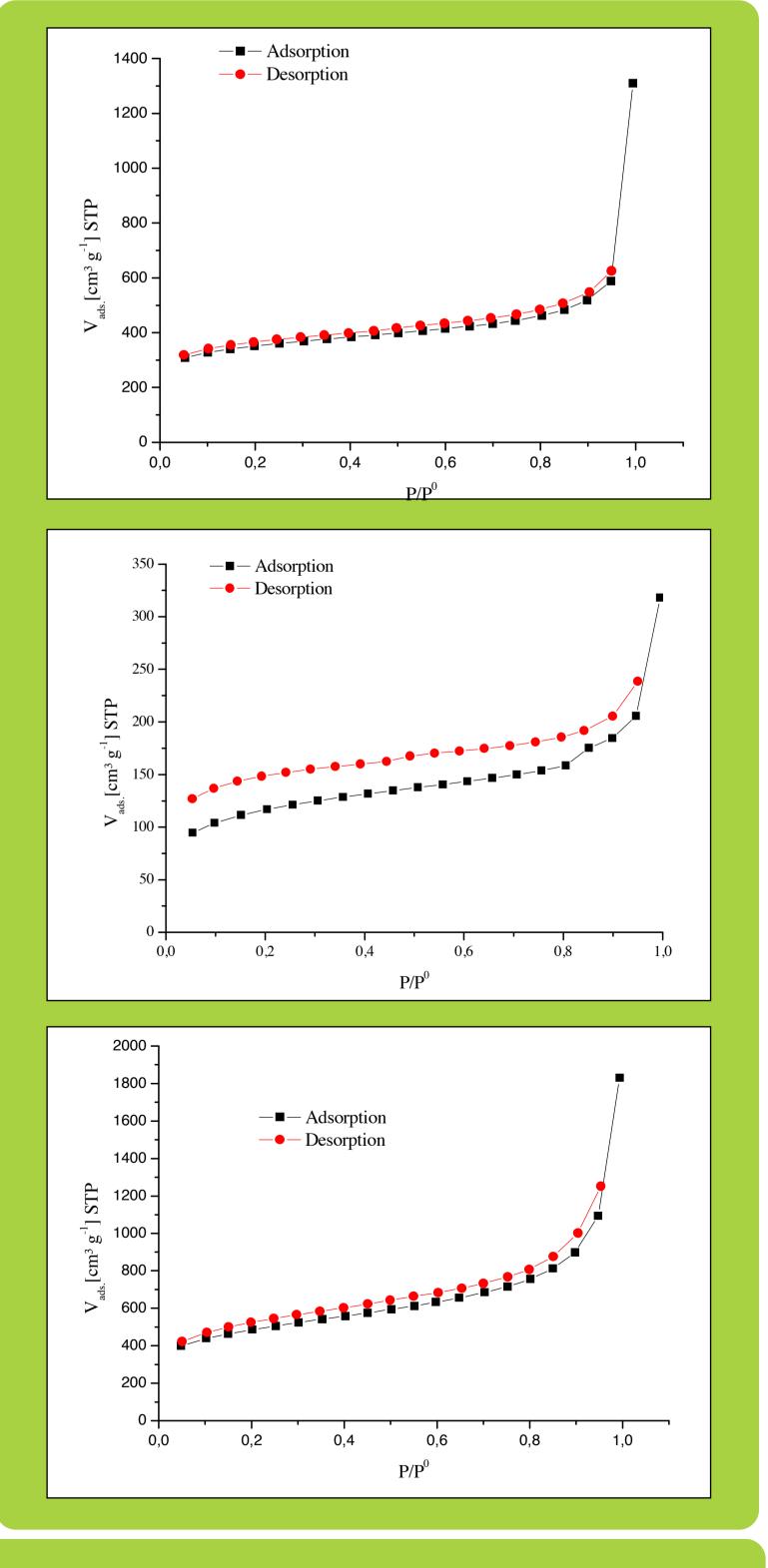
Figure 3: Idealized structure of the MPN from monomer **A** (R = phenyl) (Reaction conditions: MSA, 1,2-dichlorobenzene, 140 °C)



—■ — standard drying procedure

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_1N_2 -diphenylamino) **A** or 2,7-bis[4-(N_2N_2 -diphenylamino) **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_2 -phenyl- N_2 -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 CO_2 treatment can distinctly increase the porosity of the samples especially for MPNs made of binary monomer mixtures containing **A** and **B**. The supercritical CO_2 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 m²g⁻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.