

Microporous polyphenylenes based on diacetylaromatic compounds

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p-Diacetylbenzene from Aldrich was used without further purification. 4,4'-Diacetyldiphenyl [¹H NMR 400 MHz (CDCl₃), δ, ppm: 2.67 (s, 6H, CH₃); 7.74 (d, 4H, C₆H₄, *J* = 8.4 Hz); 8.08 (d, 4H, C₆H₄, *J* = 8.4 Hz)] were synthesized according to the procedure;¹ Mp = 193–194°C (according to the literature,² 190–191°C). 2,8-Diacetyldibenzofuran [¹H NMR 400 MHz (CDCl₃), δ, ppm: 2.76 (s, 6H, CH₃); 7.67 (d, 2H, arom., *J* = 8.6 Hz); 8.19 (dd, 2H, arom., *J*₁ = 8.6 Hz; *J*₂ = 1.8 Hz); 8.67 (d, 2H, arom., *J* = 1.6 Hz)] were synthesized according to the procedure;³ Mp = 161–162°C (according to the literature data,⁴ 161–162°C). 4,4'-Diacetyldiphenyl oxide [¹H NMR 400 MHz (CDCl₃), δ, ppm: 2.62 (s, 6H, CH₃); 7.10 (d, 4H, C₆H₄, *J* = 8.8 Hz); 8.01 (d, 4H, C₆H₄, *J* = 8.8 Hz)] were synthesized according to the procedure;¹ Mp = 101–102°C (according to the literature,⁵ 102.5°C).

Synthesis of polymer 1: 1.96 g (12 mmol) of *p*-diacetylbenzene, 7.2 ml (43.2 mmol) of ethyl orthoformate and 132 ml of benzene were placed to a flask equipped with a magnetic stirrer. Hydrogen chloride gas was passed through the reaction solution for 4 hours. The resulting gel was separated, washed with ethanol and extracted with chloroform, then dried. Yield 1.58 g.

Synthesis of polymer 2a. Hydrogen chloride gas was passed through a solution of 0.98 g (9 mmol) of *p*-diacetylbenzene, 3.6 ml (21.6 mmol) of ethyl orthoformate and 66 ml of benzene with stirring. Then, 2.4 ml (20 mmol) of acetophenone was added to the reaction mixture, and after 1 h, more 5.4 ml (32.4 mmol) of ethyl orthoformate. Hydrogen chloride was bubbled for another 1 h. The resulting product was separated, washed with ethanol and extracted with chloroform, then dried. Yield 0.83 g.

Synthesis of polymer 2b. A mixture of 0.5 g of **1**, 1.8 ml (15 mmol) of acetophenone, 3.6 ml (21.6 mmol) of ethyl orthoformate and 10 ml of benzene was stirred for 2 hours. Then gaseous hydrogen chloride was passed through the suspension with stirring for 3 hours. The resulting gel was separated washed with ethanol and extracted with chloroform, then dried. Yield 0.51 g.

Synthesis of polymer 3: 0.5 g of compound **1** was heated at 450°C in an argon atmosphere for 3 hours. Yield 0.44 g.

Synthesis of polymer 4. To a flask equipped with a magnetic stirrer 0.48 g (2 mmol) of 4,4'-diacetyldiphenyl, 1.2 ml (7.2 mmol) of ethyl orthoformate and 44 ml of benzene were placed. Hydrogen chloride gas was passed through the reaction solution for 4 hours. The resulting product was separated, washed with ethanol and extracted with chloroform, dried, then heated at 450°C in argon atmosphere for 3 hours. Yield 0.42 g.

The synthesis of polymers **5** and **6** was carried out similarly to the synthesis of product **4**.

¹H NMR spectra were recorded on a Bruker Avance-400 spectrometer with an operating frequency of 400.13 MHz. CDCl₃ was used as a solvent. The IR spectra of the samples were recorded on a Tensor-37 Bruker IR Fourier spectrometer. The reaction progress was monitored by thin layer chromatography on Silufol UV 254 plates. Silica gel 70–230 mesh, 60 A (Merck,

Germany) was used for chromatographic separation of compounds. The value of the internal specific surface was determined by the method of thermal desorption of argon on the Tsvet-211 instrument.

References

- S1. M. M. Dashevsky and B. N. Shamis, *Ukr. Khim. Zh.*, 1964, **30**, 938 (in Russian).
S2. S. W. Yuan, S. Kirklin, B. Dorney, D. J. Liu and L. P. Yu, *Macromolecules*, 2009, **42**, 1554.
S3. H. Gilman, L. C. Cheney and H. B. Willis, *J. Am. Chem. Soc.*, 1939, **61**, 951.
S4. R. C. Helgeson, *J. Chem. Soc., Chem. Commun.*, 1983, 101.
S5. R. G. Neville and R. W. Rosser, *Makromol. Chem.*, 1969, **123**, 19.

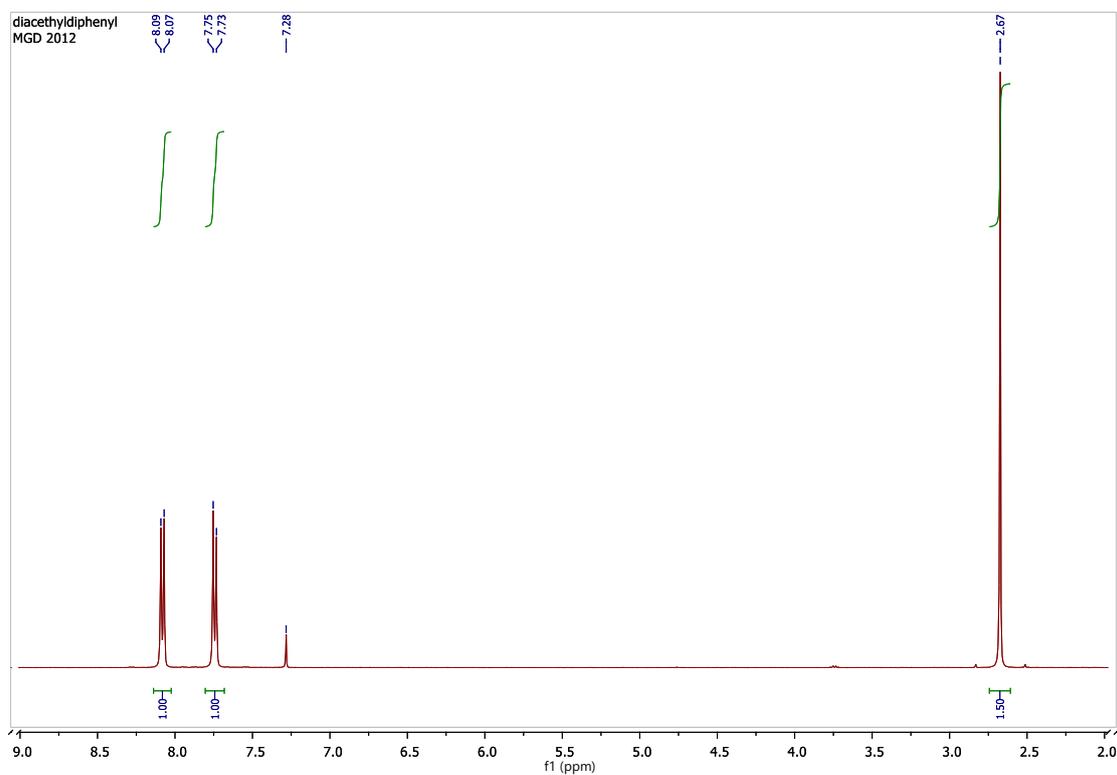


Figure S1 ¹H NMR spectrum of 4,4'-diacetyldiphenyl

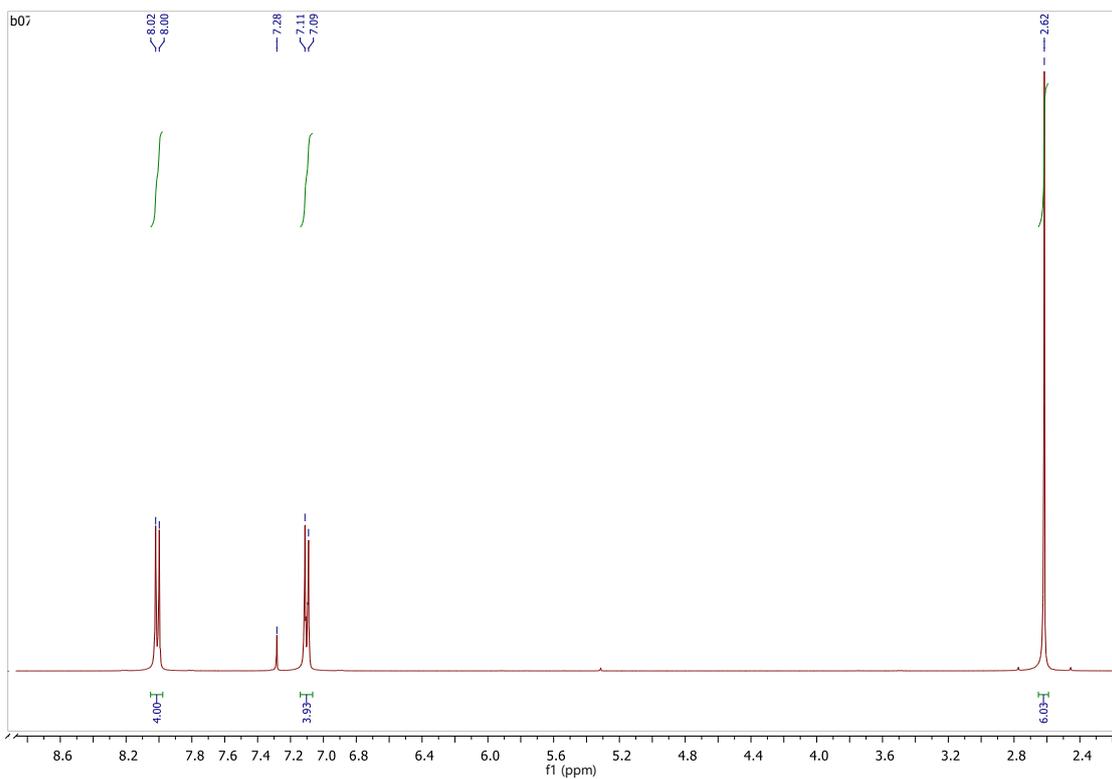


Figure S2 ^1H NMR spectrum of 4,4'-diacetyldiphenyl oxide

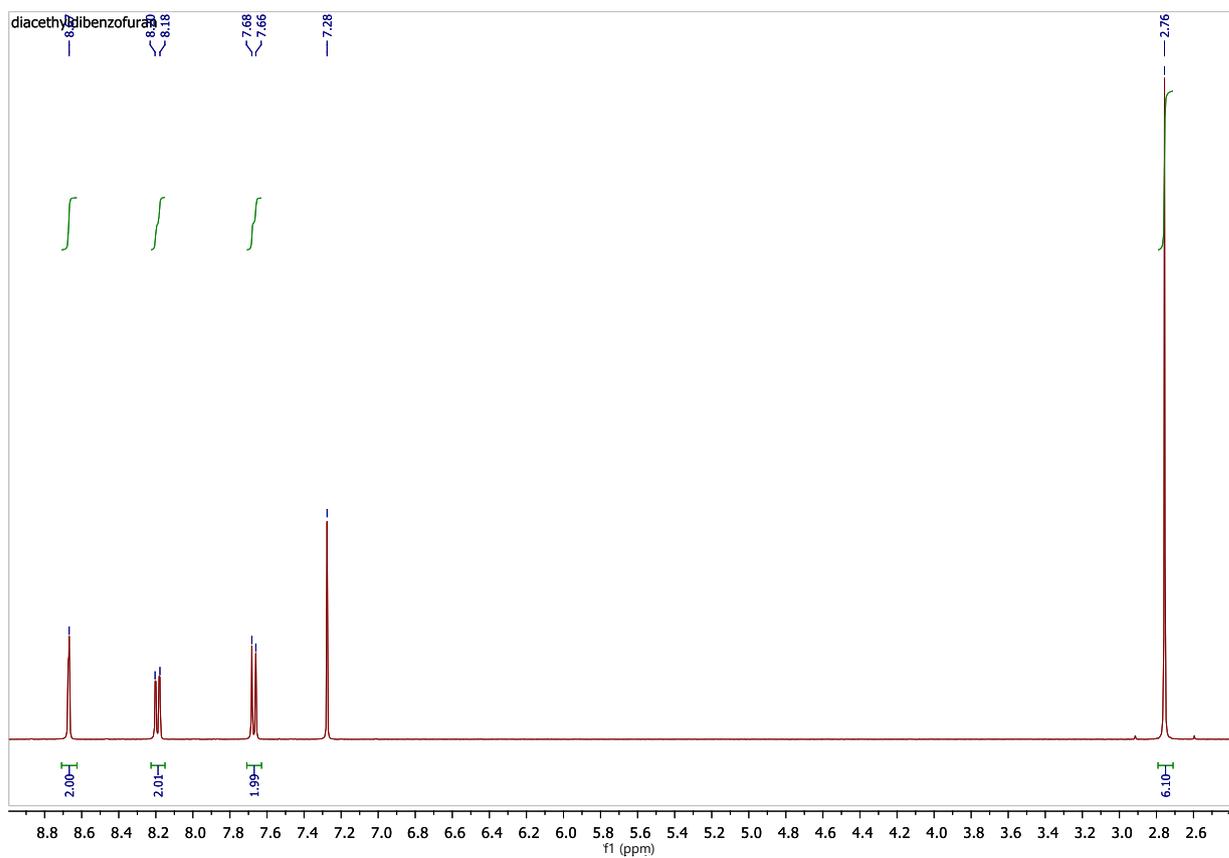


Figure S3 ^1H NMR spectrum of 2,8-diacetyldibenzofuran