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Microporous polymers based on triacetylarenes

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Materials and methods

^{1}H NMR spectra of 10 mg ml^{-1} $CDCl_3$ solutions were recorded at Bruker AVANCE 400 spectrometer with an operating frequency of 400.13 MHz at ambient temperature. Chemical shifts were given in ppm relative to tetramethylsilane (δ 0 ppm). The IR spectra were recorded on a BRUKER Vertex-70 FTI spectrometer (KBr pellet technique) from 400 to 4000 cm^{-1}.

The porous structure of the synthesized polymers was studied on a NOVA 1200e specific surface and porosity analysis unit (Quantachrome Instruments, United States). Calculations were performed using the program NOVAWin (version 11.04) with a built-in package of algorithms for calculating the basic parameters of porosity in terms of several theoretical methods based on the Brunauer–Emmett–Teller and Barrett– Joyner–Halenda (BJH) theories and a large set of calculations options based on the density functional theory (DFT). Microporous structure analysis was carried out using Dubinin–Rudushkevich and Dubinin–Astakhov methods, comparative t-method, the Moller–Plesset method, and Alpha-S method. Nitrogen was used as a sorbate gas, and the temperature of nitrogen sorption measurements was 77 K.

Polymer samples were preheated at 60 °C in vacuum in the degassing station of the NOVA 1200e analyzer for 30–60 min. The sorbate volume was measured under the following conditions: a permissible pressure deviation of 0.1 Torr and the minimum and maximum time for establishing equilibrium pressure needed to measure the value of adsorption of 60 and 240 s, respectively. To calculate the micropore volume according to the Alpha-S method, the standard carbon material isotherm was used (ACARB in the NowaWin program).[S1]

Synthesis of 1,3,5-triacetylbenzene (**1**)

Step 1. **1,3,5-Tris(trimethylsilylethynyl)benzene.** In a Schlenk tube, $Pd(PPh_3)_4$ (0.550 g, 0.6 mmol) and CuI (0.091 g, 0.477 mmol) were added with stirring to a solution of 1,3,5-tribromobenzene (5 g, 15.9 mmol) and trimethylsilylacetylene (6.25 ml, 63.5 mmol) in triethylamine (90 ml). The reaction mixture was stirred at 65 °C for 5 days (NMR monitoring). After the completion of the reaction, petroleum ether was added to the products, and the compound was separated on a short silica gel column. The fraction containing 1,3,5-tris(trimethylsilylethynyl)benzene was evaporated, dissolved in hexane, and separated on a column (silica gel, hexane). Yield: 4.14 g (71%) of 1,3,5-tris (trimethylsilylethynyl) benzene, and 0.81 g of 1,3-bis(trimethylsilylethynyl)benzene.

Step 2. **1,3,5-Triethynylbenzene.** To a solution of 1,3,5-tris(trimethylsilylethynyl)-benzene (11.6 g, 30.9 mmol) in methanol (150 ml) and THF (300 ml) aqueous KOH (10%, 100 ml) was added. The mixture was stirred for 1.5 h, then the solvents were distilled off, and ether and water were added. The organic phase was washed with water until neutral, dried over $CaCl_2$. The solvents were distilled off, hexane was added, and the product separated on a column (silica gel, hexane). Yield 4.4 g (92%). m.p. 104.5-105°C (lit.[S2] 104-105°C).

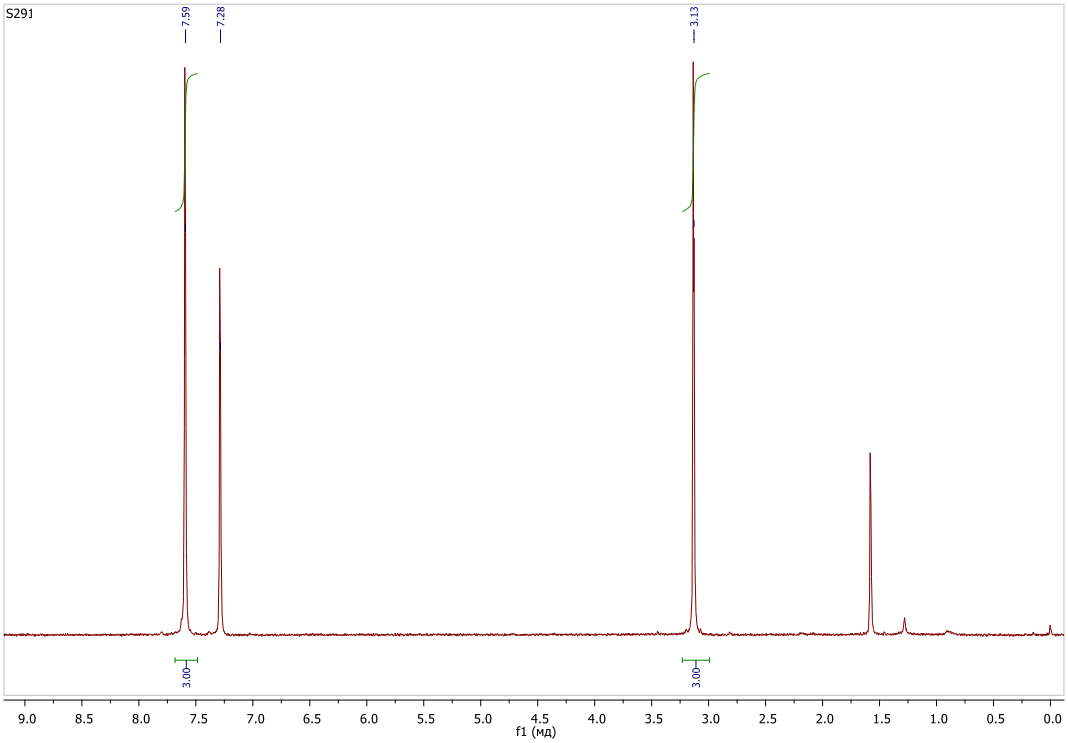

Figure S1 ^{1}H NMR 1,3,5-triethynylbenzene (400 MHz)

Step 3. A mixture of 1,3,5-triethynylbenzene (2.3 g, 15 mmol), acetic acid (22.5 ml), dichloroethane (45 ml) and *p*-toluenesulfonic acid (34 g, 60 mmol) was placed into a Schlenk tube and stirred at 80°C (bath temperature) for 2 days. The mixture was neutralized with Na_2CO_3, and the product was extracted with chloroform. The organic phase was washed with water until neutral and dried over $CaCl_2$. The solvents were evaporated. The product was isolated by column chromatography (chloroform/acetone, 25: 1). Yield 2.1 g (67%). M.p. 162-163 °C (lit.[S3] 162-163°C).

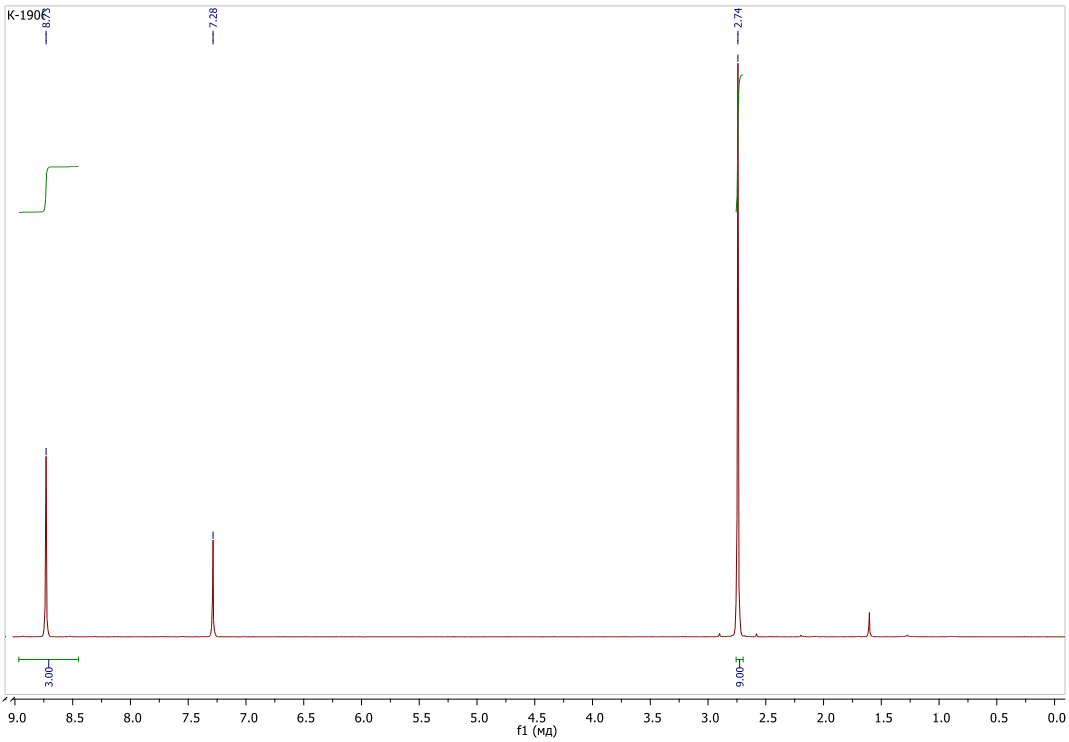

Figure S2 ^{1}H NMR 1,3,5-triacetylbenzene (400 MHz)

Synthesis of 1,3,5-triphenylbenzene. Hydrogen chloride was bubbled through a solution of acetophenone (48 ml, 0.4 M), triethyl orthoformate (80 ml, 0.48 M) and toluene (110 ml) at room temperature and stirred for 6 hours. Then ethanol (500 ml) was added. The precipitate was filtered off, washed with ethanol, and dried. Yield 28.2 g (69%). M.p. 173-175°C (lit.[S4] 172° C).

Synthesis of 1,3,5-tris(4-acetylphenyl)benzene (**2a**). A solution of AcCl (2.15 ml, 30 mmol) in dichloroethane (5 ml) was added dropwise to a suspension of $AlCl_3$ (4.13 g, 31 mmol) in dichloroethane (5 ml) with stirring at ~5 °C for 15 min under the same conditions. Then a solution of 1,3,5-triphenylbenzene (3.06 g, 10 mmol) in dichloroethane (60 ml) was added dropwise over 30 min. The cooling bath was allowed to warm to room temperature. The reaction mixture was stirred for another 6 h, then it was poured with vigorous stirring into ice water acidified with hydrochloric acid. The resulting mixture was extracted with chloroform. The organic layer was washed with water until neutral reaction and dried over $CaCl_2$. Volatile components were evaporated. The product was isolated by column chromatography (chloroform/acetone, 25:1). Yield 2.9 g (67%). M.p. = 245°C.

Synthesis of 4-phenoxyacetophenone. A two-necked flask equipped with a magnetic stirrer was charged with $AlCl_3$ (20 g, 0.15 mol) and dichloromethane (18 ml). To this mixture at -50 °C and vigorous stirring acetyl chloride (10.7 ml, 0.15 mol) was added. The resulting acylation complex was added dropwise to a solution of diphenyl oxide (17 g, 0.1 mol) in dichloromethane (12 ml) cooled to -50 °C. The mixture was stirred for 2 hours at -50 °C and then for another 2 hours at room temperature. After that, the reaction mixture was poured into ice water, acidified with hydrochloric acid. The resulting mixture was extracted with chloroform, after which the organic phase was washed with water until neutral and then dried over calcium chloride. After distilling off the solvent, the title product was separated using column chromatography (silica gel, chloroform). The yield is 5 g (24%). M.p. 51 °C (lit.[S5] 49-50.5 °C).

Synthesis of 1,3,5-tris(4-phenoxyphenyl)benzene. Through a solution of 4-phenoxy-acetophenone (5 g, 23.6 mmol) and triethyl orthoformate (4.7 ml, 28.2 mmol) in benzene (14 ml), HCl gas was passed at room temperature with stirring for 3 hours. The reaction mixture was then poured into ethanol. The precipitate was filtered off. The title product was separated by column chromatography (silica gel, - petroleum ether/CH_2Cl_2, 1:2). The yield is 2.33 g (51%). M.p. = 148-150 ° C. MS: 291 (14), 582 (M +) (100), 584 (14).

Synthesis of 1,3,5-tris[4-(4-acetylphenoxy)phenyl]benzene (**2b**). A two-necked flask equipped with a magnetic stirrer was charged with $AlCl_3$ (1.6 g, 12 mmol) and dichloroethane 1.6 ml). Acetyl chloride (0.9 ml, 12.6 mmol) was added dropwise to the resulting mixture at -10 °C and vigorous stirring. A solution of 1,3,5-tris(4-phenoxyphenyl)benzene (1.9 g, 2 mmol) of in dichloroethane (12 ml) was added dropwise to the resulting complex cooled to -50 °C through a dropping funnel. The reaction mixture was stirred for 1 hour at -30 °C. After that, the mixture was poured into ice water acidified with hydrochloric acid. The resulting mixture was extracted with $CHCl_3$, the combined organic phase was washed with water until neutral, then dried over $CaCl_2$. After distilling off the solvents, the title product was separated by column chromatography (silica gel, $CHCl_3$/acetone, 40: 1). Yield 1.5 g (65%). M.p. = 216-218 °C.

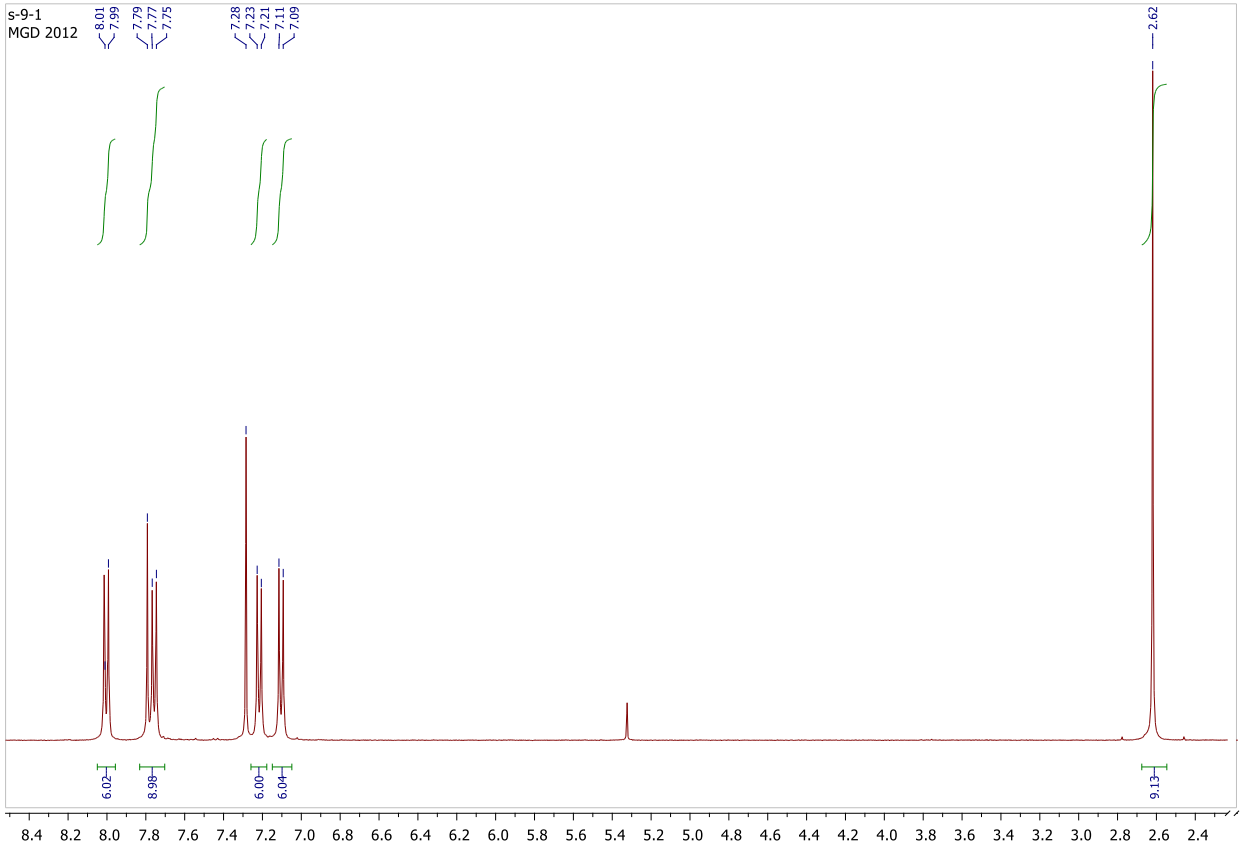

Figure S3 ^{1}H NMR of 1,3,5-tris[4-(4-acetylphenoxy)phenyl]benzene.

Synthesis of polyphenylene based on 1,3,5-triacetylbenzene (**P1**) Hydrogen chloride was bubbled through a mixture of 1,3,5-triacetylbenzene (0.408 g, 2 mmol), triethyl orthoformate (1.2 ml, 7.2 mmol) and toluene (11 ml) with stirring at room temperature for 2.5 h. Then the reaction mixture was kept in a closed flask for 21.5 h. The resulting polymer was filtered off, washed with chloroform and ethanol, extracted with chloroform, and dried. Yield 0.315 g.

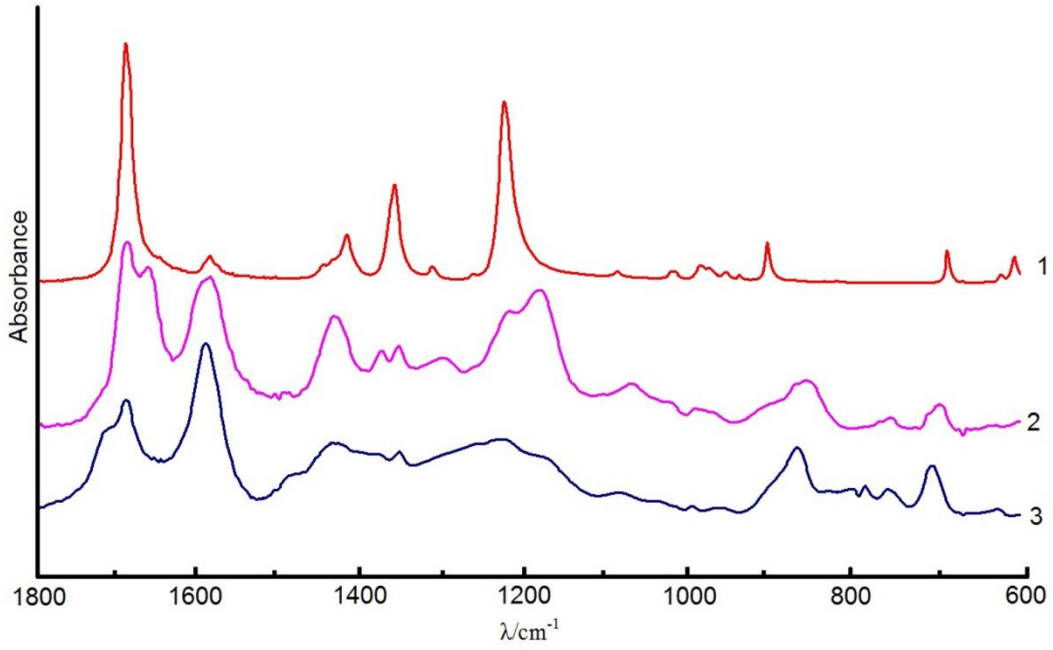

Figure S4. IR spectra of: monomer **1** (*1*), **P1** (*2*), **Q1** (*3*)

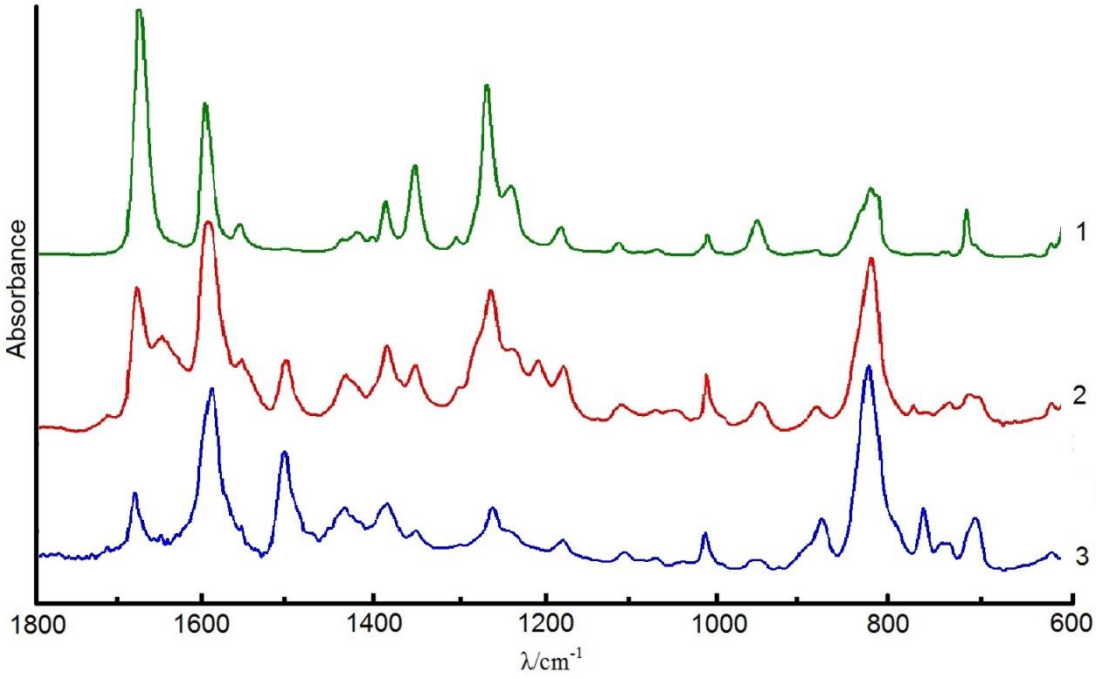

Figure S5. IR spectra of: monomer **2a** (*1*), **P2** (*2*), **Q2** (*3*)

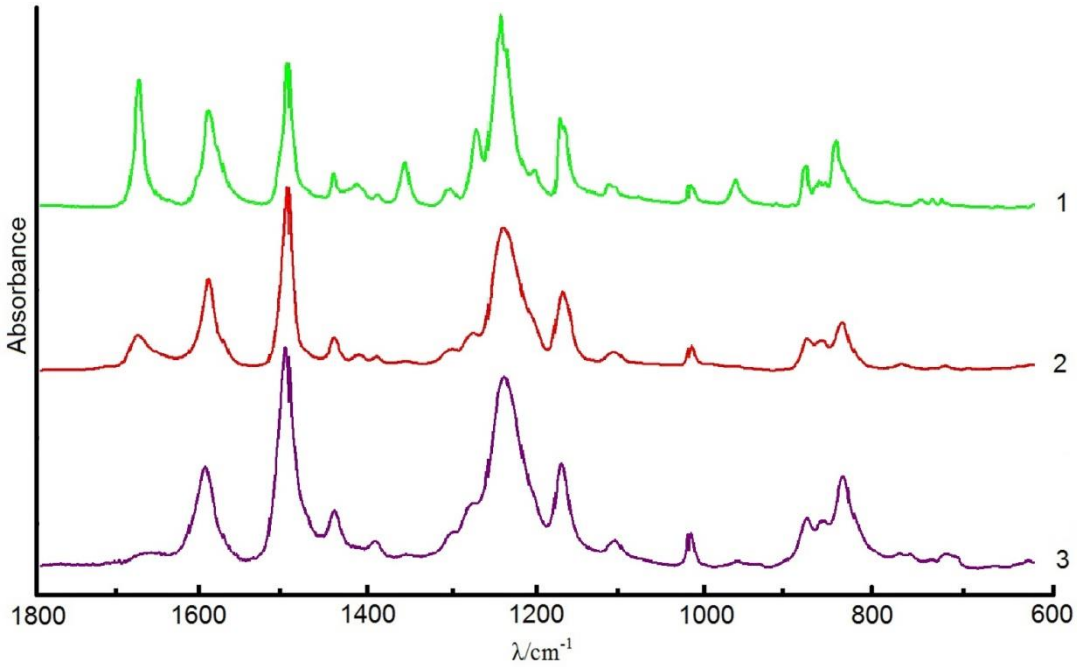

Figure S6. IR spectra of: monomer **2b** (*1*), **P3** (*2*), **Q3** (*3*)

References

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