Supporting Information

Lignin-Inspired Polymers with High Glass Transition Temperature and Solvent Resistance from 4-hydroxybenzo-, Vanillo- and Syringonitrile Methacrylates

Olivier Bonjour¹, Hannes Nederstedt¹, Monica V. Arcos-Hernandez¹, Siim Laanesoo², Lauri Vares², Patric Jannasch¹,²,*

¹ Centre for Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden
² Institute of Technology, University of Tartu, Nooruse 1, Tartu 50411, Estonia

*Corresponding author e-mail: patric.jannasch@chem.lu.se

Number of pages in Supporting Information: 22
Number of tables in Supporting Information: 2
Number of figures in Supporting Information: 10
Table of Contents

Experimental section .................................................................................................................. 3
  Materials ................................................................................................................................. 3
  Analytical Methods ................................................................................................................. 3
  Thermogravimetry and calorimetry ......................................................................................... 3
  Melt rheology ........................................................................................................................... 3
  Synthesis of compounds ......................................................................................................... 3
    4-Hydroxybenzonitrile 2a ...................................................................................................... 3
    4-Hydroxy-3,5-dimethoxybenzonitrile (syringonitrile) 2c ...................................................... 4
    4-Cyano-2-methoxyphenyl methacrylate (benzonitrile methacrylate) BM ......................... 4
    4-Cyano-2,6-dimethoxyphenyl methacrylate (vanillinitrile methacrylate) VM .................. 4
    Poly(4-cyano-2-methoxyphenyl methacrylate) [poly(benzonitrile methacrylate)] PBM .......... 5
    Poly(4-cyano-2-methoxyphenyl methacrylate) [poly(vanillinitrile methacrylate)] PVM .......... 5
    Poly[styrene-co-(4-cyano-2-methoxyphenyl methacrylate)] PSVM-14 ................................. 5
    Poly[styrene-co-(4-cyano-2-methoxyphenyl methacrylate)] PSVM-28 ............................... 6
    Poly[styrene-co-(4-cyano-2-methoxyphenyl methacrylate)] PSVM-45 ............................... 6
    Poly(4-cyano-2,6-dimethoxyphenyl methacrylate) [poly(syringonitrile methacrylate)] PSM ... 6
    Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-16 ......................... 6
    Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-25 ......................... 7
    Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-35 ......................... 7
    Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-42 ......................... 7
    Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-50 ......................... 7
    Poly[(methyl 2-methylpropenoate)-co-(4-cyano-2-methoxyphenyl methacrylate)] PMVM-18 ... 8
    Poly[(methyl 2-methylpropenoate)-co-(4-cyano-2-methoxyphenyl methacrylate)] PMVM-41 .... 8

NMR Spectra ............................................................................................................................ 9

TGA Traces .............................................................................................................................. 15

Flory-Fox plot ........................................................................................................................... 17

SEC Curves .............................................................................................................................. 18

Evaluation of the Solubility of Polybenzonitrile methacrylates ............................................... 20

Summary of previously reported $T_g$s of lignin-based polymethacrylates ............................. 21
Experimental section

Materials
All reagents and solvents were obtained from commercial sources and used without further purification. The monomer synthesis steps were monitored by thin-layer chromatography (TLC, silica gel 60 F\textsubscript{254}), and TLC plates were visualized using a UV lamp. Aluminum oxide (active basic, particle size 0.063-0.200 mm (70-230 mesh ASTM)) was used in the flash chromatography.

Analytical Methods
Nuclear Magnetic Resonance (NMR) spectroscopy was performed on a Bruker DR X400 spectrometer at 400.13 MHz proton frequency and 100.62 MHz carbon frequency. The formation of the polymers was determined by the decrease of the double bond signals of the methacrylate moiety. The molecular weight of the polymers was determined by Size Exclusion Chromatography (SEC) using THF or DMF/0.05 M LiBr as eluent at 40 °C. The instrument included Shodex columns coupled in series (KF-805, -804 and -802.5 for THF and KD-804 and -802.5 for DMF) placed in a Shimadzu CTO-20A prominence column oven, a Shimadzu RID-20A refractive index detector, with Shimadzu LabSolution software. Calibration was done by using poly(ethylene oxide) standards (\(M_n = 3.86, 21.16, 49.39\) and 96.1 kg/mol). All samples were run at an elution rate of 1 mL/min.

Thermogravimetry and calorimetry
Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500. Samples from 1-6 mg were heated to 600 °C at a rate of 10 °C/min under nitrogen flux (60 mL/min). The thermal decomposition temperature (\(T_{d,95\%}\)) was determined at 5% loss of the total weight. Differential scanning calorimetry (DSC) measurements were performed on TA Instruments DSC Q2000. Samples from 1-10 mg were first heated up to 170-250 °C (depending on their respective thermal decomposition temperature) at a rate of 10 °C/min. They were kept at this temperature for 2 min, then cooled down to -50 °C and kept isothermal for 2 min, before being heated up again to the previous temperature, at the same heating rate.

Melt rheology
Dynamic rheology measurements were performed with TA Instruments Advanced Rheometer AR2000 ETC. The experiments were made using parallel plates (\(\phi = 15\) mm). Discs of PSVM-14, PSVM-28, PSSM-25 and PMVM-18 (\(\phi = 15\) mm, \(t = 1\) mm) were hot-pressed between two aluminum plates using a hydraulic press (Specac, GS15011) at 150 °C during 5 min, and finally cooled to room temperature. A time sweep was carried out during 8 h at 150 °C, at a frequency of 1 Hz at 0.1% strain, which was within the linear viscoelastic region.

Synthesis of compounds
4-Hydroxybenzonitrile 2a
To a 250 mL round-bottom flask equipped with a magnetic stirrer, 4-hydroxybenzaldehyde 1a (4.000 g, 32.8 mmol, 1.0 equiv.) and hydroxylamine-\(O\)-sulfonic acid (4.075 g, 36.0 mmol, 1.1 equiv.) were dissolved in a mixture of water (160 mL) and acetic acid (1.970 g, 32.8 mmol, 1.0 equiv.) cooled with an ice bath. The reaction mixture was stirred at 50 °C for 6 h. After completion, the reaction mixture was quenched by
a 10% NaHCO₃ aqueous solution, until no gas release was observed. The product was extracted by EtOAc (3 × 60 mL). The organic phases were gathered, dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. The residue was purified by recrystallization in heptane. The product was dried carefully under vacuum to afford 3.180 g of a light brown powder (yield: 82%). ¹H NMR (400.13 MHz, CDCl₃) δ, ppm: 6.30 (s, 1H), 6.91-6.95 (m, 2H), 7.54-7.58 (m, 2H), melting temperature: Tₘ = 112 °C.

4-Hydroxy-3,5-dimethoxybenzonitrile (syringonitrile) 2c
To a 250 mL round-bottom flask equipped with a magnetic stirrer, 4-hydroxy-3,5-dimethoxybenzaldehyde 1c (5.000 g, 27.4 mmol, 1.0 equiv.) and hydroxylamine-O-sulfonic acid (3.414 g, 30.2 mmol, 1.1 equiv.) were dissolved in a mixture of water (50 mL) and acetic acid (1.648 g, 27.4 mmol, 1.0 equiv.) cooled with an ice bath. The reaction mixture was stirred at 50 °C for 6 h. After completion, the reaction mixture was quenched by 10% NaHCO₃ until no gas release was observed. The product was extracted by EtOAc (3 × 30 mL). The organic phases were gathered, dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. The residue was purified by recrystallization in heptane. The product was dried carefully under vacuum to afford 3.874 g of a light brown powder (yield: 79%). ¹H NMR (400.13 MHz, CDCl₃) δ, ppm: 3.90 (s, 6H), 6.02 (s, 1H), 6.85 (s, 2H); melting temperature: Tₘ = 128 °C.

4-Cyanophenyl methacrylate (benzonitrile methacrylate) BM 3a
To a 25 mL round-bottom flask equipped with a magnetic stirrer, 4-hydroxybenzonitrile 2a (2.90 g, 24.3 mmol, 1.0 equiv.) and DMAP (0.06 g, 0.49 mmol, 0.02 equiv.) were dissolved in EtOAc (4.0 mL). The flask was sealed and purged with vacuum/N₂ cycles. Methacrylic anhydride (3.79 g, 24.6 mmol, 1.01 equiv.) was added dropwise to the reaction mixture. The flask was purged again as described above, and the reaction mixture was then heated at 65 °C for 2 h. The obtained precipitate was filtered and washed with EtOAc (25 mL). The filtrate was washed with a saturated NaHCO₃ aqueous solution, until no gas release was observed. The organic phase was then washed with sodium hydroxide (2.5 M, 25 mL), hydrochloric acid (1 M, 25 mL) and water (25 mL). The organic phase was dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. The product was dried carefully under vacuum to afford 3.180 g (from precipitate and filtrate) of a white powder (yield: 70%). ¹H NMR (400.13 MHz, DMSO-d₆) δ, ppm: 2.00 (m, 3H), 5.93-5.95 (m, 1H), 6.30-6.31 (m, 1H), 7.41-7.45 (m, 2H), 7.91-7.95 (m, 2H), ¹³C NMR (100.62 MHz, DMSO-d₆) δ, ppm: 17.9, 108.8, 118.4, 123.3, 128.5, 134.0, 134.9, 154.1, 164.7; ¹H NMR (400 MHz, CDCl₃) δ, ppm: 2.06 (m, 3H), 5.82 (m, 1H), 6.38 (m, 1H), 7.25-7.29 (m, 2H), 7.69-7.72 (m, 2H), ¹³C NMR (100.62 MHz, CDCl₃) δ, ppm: 18.4, 109.8, 118.4, 122.9, 128.5, 133.8, 135.4, 154.4, 165.0; melting temperature: decomposition before reaching melting.

4-Cyano-2-methoxyphenyl methacrylate (vanillonitrile methacrylate) VM 3b
To a 100 mL round-bottom flask equipped with a magnetic stirrer, vanillonitrile 2b (21.08 g, 0.14 mol, 1.0 equiv.) and DMAP (0.35 g, 2.8 mmol, 0.02 equiv.) were dissolved in EtOAc (40 mL). The flask was sealed and purged with vacuum/N₂ cycles. Methacrylic anhydride (22.01 g, 0.14 mol, 1.01 equiv.) was added dropwise to the reaction mixture. The flask was purged again as described above, and the reaction mixture was then heated at 55 °C for 24 h. After completion, EtOAc (25 mL) were added to the reaction mixture, which was subsequently washed with a saturated NaHCO₃ aqueous solution, until no gas release was observed. The organic phase was then washed with sodium hydroxide (2.5 M, 25 mL), hydrochloric acid (1 M, 25 mL) and water (25 mL). The organic phase was dried over anhydrous sodium sulfate, filtered and
concentrated with a rotary evaporator. The product was dried carefully under vacuum to afford 29.197 g of a white powder (yield: 89%). 1H NMR (400.13 MHz, DMSO-d$_6$) δ, ppm: 1.99 (m, 3H), 3.84 (s, 3H), 5.93-5.94 (m, 1H), 6.29 (m, 1H), 7.37-7.39 (d, J = 8.1 Hz, 1H), 7.48-7.50 (dd, J = 1.8 and 8.2 Hz, 1H), 7.67 (d, J = 1.8 Hz, 1H), 13C NMR (100.62 MHz, DMSO-d$_6$) δ, ppm: 18.0, 56.6, 109.7, 116.5, 118.4, 124.3, 125.5, 128.6, 134.5, 143.4, 151.5, 164.2; 1H NMR (400 MHz, CDCl$_3$) δ, ppm: 2.06 (m, 3H), 3.86 (s, 3H), 5.79-5.81 (m, 1H), 6.37 (m, 1H), 7.16-7.18 (d, J = 8.16 Hz, 1H), 7.21 (d, J = 1.77 Hz, 1H), 7.29-7.31 (dd, J = 1.80 and 8.12 Hz, 1H), 13C NMR (100.62 MHz, CDCl$_3$) δ, ppm: 18.5, 56.4, 110.6, 115.8, 118.5, 124.2, 125.5, 128.3, 135.2, 144.1, 152.0, 164.7; melting temperature: decomposition before reaching melting

4-Cyano-2,6-dimethoxyphenyl methacrylate (syringonitrile methacrylate) SM 3c

To a 100 mL round-bottom flask equipped with a magnetic stirrer, 4-hydroxy-3,5-dimethoxybenzonitrile 2c (2.862 g, 15.97 mmol, 1.0 equiv.) and DMAP (39.4 mg, 0.323 mmol, 0.02 equiv.) were dissolved in degassed acetonitrile (2 mL). Methacrylic anhydride (2.487 g, 16.13 mmol, 1.01 equiv.) was added dropwise to the reaction mixture. The flask was purged again as described above, and the reaction mixture was then heated at 65 °C for 24 h. The precipitate was filtered and washed with cold EtOAc (25 mL). SM was further purified by aluminum oxide column chromatography, with heptane as eluent, to remove residual acid and phenol. The product was dried carefully under vacuum to afford 2.915 g of a white powder (yield: 74%). 1H NMR (400.13 MHz, CHCl$_3$) δ, ppm: 2.06 (m, 3H), 3.83 (s, 3H), 5.98 (m, 1H), 6.37 (m, 1H), 6.89 (s, 2H), 13C NMR (100.62 MHz, CDCl$_3$) δ, ppm: 18.5, 56.4, 110.6, 115.8, 118.5, 124.2, 125.5, 128.3, 135.2, 144.1, 152.0, 164.7; melting temperature: decomposition before reaching melting

Poly(4-cyanophenyl methacrylate) [poly(benzonitrile methacrylate)] PBM

In a schlenk flask, 10 mL of acetonitrile were degassed with vacuum/N$_2$ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyanophenyl methacrylate BM 3a (0.650 g, 3.475 mmol, 1.0 equiv.) were dissolved in degassed aceton (4.00 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (3.0 mg) were dissolved in degassed acetonitrile (2 mL). 1 mL of the AIBN solution is introduced in the flask with the dissolved monomer, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.316 g (49%).

Poly(4-cyano-2-methoxyphenyl methacrylate) [poly(vanillonitrile methacrylate)] PVM

In a schlenk flask, 6 mL of DMSO were degassed with vacuum/N$_2$ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2-methoxyphenyl methacrylate VM 3b (0.500 g, 2.302 mmol, 1.0 equiv.) were dissolved in degassed DMSO (2.00 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (3.22 mg) were dissolved in degassed DMSO (2 mL). 1.00 mL of the AIBN solution were introduced in the flask with the dissolved monomer, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.360 g (72%).

Poly[styrene-co-(4-cyano-2-methoxyphenyl methacrylate)] PSVM-14

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N$_2$ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2-methoxyphenyl methacrylate VM 3b (0.094 g, 0.433
mmol) and styrene (0.406 g, 3.897 mmol) were dissolved in degassed DMSO (4.56 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (20 mg) were dissolved in degassed DMSO (2 mL). 1.42 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH. The formed white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.337 g (67%).

Poly[styrene-co-(4-cyano-2-methoxyphenyl methacrylate)] PSVM-28

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2-methoxyphenyl methacrylate VM 3b (0.171 g, 0.789 mmol) and styrene (0.329 g, 3.155 mmol) were dissolved in degassed DMSO (4.20 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (20 mg) were dissolved in degassed DMSO (2 mL). 1.29 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.361 g (72%).

Poly[styrene-co-(4-cyano-2-methoxyphenyl methacrylate)] PSVM-45

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2-methoxyphenyl methacrylate VM 3b (0.338 g, 1.556 mmol) and styrene (0.162 g, 1.556 mmol) were dissolved in degassed DMSO (3.42 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (20 mg) were dissolved in degassed DMSO (2 mL). 1.02 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.487 g (97%).

Poly(4-cyano-2,6-dimethoxyphenyl methacrylate) [poly(syringonitrile methacrylate)] PSM

In a schlenk flask, 6 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2,6-dimethoxyphenyl methacrylate SM 3c (0.500 g, 2.022 mmol, 1.0 equiv.) were dissolved in degassed DMSO (2.56 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (30 mg) were dissolved in degassed DMSO (2 mL). 0.44 mL of the AIBN solution were introduced in the flask with the dissolved monomer, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.463 g (93%).

Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-16

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2,6-dimethoxyphenyl methacrylate SM 3c (0.104 g, 0.422 mmol) and styrene (0.396 g, 3.798 mmol) were dissolved in degassed DMSO (2.5 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (83 mg) were dissolved in degassed DMSO (2.5 mL). 0.5 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated
in MeOH. The formed white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.398 g (80%).

**Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-25**

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2,6-dimethoxyphenyl methacrylate SM 3c (0.186 g, 0.753 mmol) and styrene (0.314 g, 3.013 mmol) were dissolved in degassed DMSO (2.5 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (83 mg) were dissolved in degassed DMSO (2.5 mL). 0.5 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.351 g (70%).

**Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-35**

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2,6-dimethoxyphenyl methacrylate SM 3c (0.252 g, 1.019 mmol) and styrene (0.248 g, 2.379 mmol) were dissolved in degassed DMSO (2.5 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (83 mg) were dissolved in degassed DMSO (2.5 mL). 0.5 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.453 g (91%).

**Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-42**

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2,6-dimethoxyphenyl methacrylate SM 3c (0.306 g, 1.239 mmol) and styrene (0.194 g, 1.859 mmol) were dissolved in degassed DMSO (2.5 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (83 mg) were dissolved in degassed DMSO (2.5 mL). 0.5 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.488 g (98%).

**Poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-50**

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2,6-dimethoxyphenyl methacrylate SM 3c (0.352 g, 1.423 mmol) and styrene (0.148 g, 1.423 mmol) were dissolved in degassed DMSO (2.5 mL) and degassed again as before. In a vial, azobisisobutyronitrile (AIBN) (83 mg) were dissolved in degassed DMSO (2.5 mL). 0.5 mL of the AIBN solution were introduced in the flask with the dissolved monomers, and degassed again as before. The reaction mixture was then heated at 60 °C for 24 h. The resulting material was precipitated in MeOH, and the white powder was filtered off and washed repeatedly with MeOH before drying at 50 °C under vacuum, yielding 0.433 g (89%).
Poly[(methyl 2-methylpropenoate)-co-(4-cyano-2-methoxyphenyl methacrylate)] PMVM-18

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. In another schlenk flask, 20 mL of methyl methacrylate (MMA) were degassed with the same procedure. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2-methoxyphenyl methacrylate VM 3b (0.191 mg, 0.880 mmol), MMA (0.63 mL) and DMSO (1.00 mL) were placed under N₂ atmosphere. In a volumetric flask (10 mL), azobisisobutyronitrile (AIBN) (0.500 mg) were dissolved in degassed MMA. 0.23 mL of the AIBN solution were introduced in the reaction vessel and degassed again as before (MMA 0.809 g, 7.920 mmol in total; AIBN 11.56 mg, 0.0704 mmol, 0.8 mol%). The reaction mixture was then heated at 60 °C for 17 h. The resulting material was dissolved in CHCl₃ (20 mL) and then precipitated in MeOH (200 mL). The formed white fibers were filtered off on Büchner and washed repeatedly with MeOH. The solid was dissolved again with CHCl₃ and concentrated with a rotary evaporator. The residue was dried at 50 °C under vacuum, yielding 0.93 g (93%).

Poly[(methyl 2-methylpropenoate)-co-(4-cyano-2-methoxyphenyl methacrylate)] PMVM-41

In a schlenk flask, 10 mL of DMSO were degassed with vacuum/N₂ cycles at 40 °C. In another schlenk flask, 20 mL of methyl methacrylate (MMA) were degassed with the same procedure. To a 25 mL schlenk flask equipped with a magnetic stirrer, 4-cyano-2-methoxyphenyl methacrylate VM 3b (0.477 mg, 2.195 mmol), MMA (0.37 mL) and DMSO (0.99 mL) were placed under N₂ atmosphere. In a volumetric flask (10 mL), azobisisobutyronitrile (AIBN) (0.500 mg) were dissolved in degassed MMA. 0.19 mL of the AIBN solution were introduced in the reaction vessel and degassed again as before (MMA 0.523 g, 5.123 mmol in total; AIBN 9.61 mg, 0.0585 mmol, 0.8 mol%). The reaction mixture was then heated at 60 °C for 23 h. The resulting material was dissolved in CHCl₃ (20 mL) and then precipitated in MeOH (200 mL). The white fibers were filtered off on Büchner and washed repeatedly with MeOH. The solid was dissolved again with CHCl₃ and concentrated with a rotary evaporator. The residue was dried at 50 °C under vacuum, yielding 0.63 g (63%).
Figure S1. $^1$H NMR spectrum of 4-hydroxy-3,5-dimethoxybenzonitrile (syringonitrile) 2c (*indicates heptane signals).
Figure S2. $^1$H NMR spectrum of 4-cyanophenyl methacrylate (4-hydroxybenzonitrile methacrylate) BM.
Figure S3. $^1$H NMR spectrum of 4-cyano-2-methoxyphenyl methacrylate (vanillonitrile methacrylate) VM.
Figure S4. $^1$H NMR spectrum of 4-cyano-2,5-dimethoxyphenyl methacrylate (syringonitrile methacrylate) SM.
Figure S5. $^1$H NMR spectrum of poly[styrene-co-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-16. Signals b and c were used to determine the molar composition of the copolymers (*indicates DMF signals).
Figure S6. $^1$H NMR spectrum of poly(methyl methacrylate) synthesized using the same procedure as the PMVM series. Signals a, b and c were used to determine the $rr$, $rm$ and $mm$ triad fractions, respectively.
TGA Traces

Figure S7. TGA traces of: (a) homopolymer PBM, PVM and PSM, (b) the PSSM series, (c) the PSVM series, and (d) the PMVM series under N$_2$ atmosphere at 10 °C min$^{-1}$. 
Figure S8. TGA derivative traces of: (a) homopolymer PBM, PVM and PSM, (b) the PSSM series, (c) the PSVM series, and (d) the PMVM series under N₂ atmosphere at 10 °C min⁻¹.
Flory-Fox plot

Figure S9. 1/$T_g$ of the homopolymers and copolymers versus the weight fraction of nitrile-containing monomer. The fitted linear equations $y = ax + b$ are shown as dashed lines, where $a = 1/T_g(1) - 1/T_g(2)$ and $b = 1/T_g(2)$, with (1) referring to the nitrile containing polymer and (2) to PS or PMMA, respectively. The obtained parameters $a$ and $b$ for the three copolymer series are coherent with the theoretical values predicted using the Flory-Fox model.
SEC Curves (continued on next page).

(a) 

(b) 

(c)
Figure S10. SEC of THF solutions of: (a) homopolymer PVM and PSM, (b) the PSSM series, (c) the PSVM series and (d) the PMVM series. “Intensity” is the differential refractive index (dRI) of the RI detector in arbitrary units. SEC in DMF of (a’) homopolymers PBM, PVM and PSM.
**Evaluation of the Solubility of Polybenzonitrile methacrylates**

The solubility of the different polybenzonitrile methacrylates was investigated by mixing small samples (about 5 mg) with a range of selected solvents (1 mL). The mixture was stirred for 24 h at room temperature. The results of the dissolution tests were divided into two categories, soluble and insoluble, based on visual inspection. If the samples were found to be completely dissolved, they were considered as soluble; if not, they were considered as nonsoluble.

**Table S1.** Solubility of the nitrile-containing polymers at 21 °C.

| Polymer | H2O | MeOH | 1-BuOH | DMSO | THF | Et2O | ACN | CHCl3 | Toluene |
|---------|-----|------|--------|------|-----|------|-----|-------|---------|
|         | $\delta$=48 (s) | $\delta$=43 (s) | $\delta$=23 (s) | $\delta$=25 (m) | $\delta$=19 (m) | $\delta$=15 (m) | $\delta$=24 (p) | $\delta$=19 (p) | $\delta$=18 (p) |
| PS      | -   | -    | -      | +    | +   | -    | +   | -     | +       |
| PBM     | -   | -    | -      | +    | -   | -    | -   | -     | -       |
| PSVM-14 | -   | -    | -      | +    | +   | -    | +   | -     | +       |
| PSVM-28 | -   | -    | -      | +    | +   | -    | -   | +     | +       |
| PSVM-45 | -   | -    | -      | +    | +   | -    | -   | +     | -       |
| PVM     | -   | -    | -      | +    | +   | -    | -   | -     | -       |
| PSSM-16 | -   | -    | -      | +    | -   | -    | +   | +     | +       |
| PSSM-25 | -   | -    | -      | +    | +   | -    | -   | +     | -       |
| PSSM-35 | -   | -    | -      | +    | +   | -    | -   | +     | -       |
| PSSM-42 | -   | -    | -      | +    | +   | -    | -   | +     | -       |
| PSSM-50 | -   | -    | -      | +    | +   | -    | -   | +     | -       |
| PSM     | -   | -    | -      | +    | +   | -    | +   | -     | +       |
| PMMA    | -   | -    | -      | +    | +   | -    | +   | +     | +       |
| PMVM-18 | -   | -    | -      | +    | -   | +    | +   | +     | +       |
| PMVM-41 | -   | -    | -      | +    | -   | -    | +   | -     | +       |

*The symbols “+” and “-” indicate solubility and nonsolubility, respectively. Solubility parameters ($\delta$, MP$^{1/2}$) were obtained from the *Polymer Handbook*, (J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, D. Bloch. *Polymer Handbook, 4th ed.*, John Wiley and Sons, New York, 1999), and the letters s, m and p denote strongly, moderately, and poorly hydrogen-bond-forming solvents, respectively.*
Summary of previously reported $T_g$s of lignin-based polymethacrylates.

Table S2. $T_g$s of lignin-based methacrylate polymers reported in the literature (continued on next page).

| Structure | Name of phenolic moiety | $M_n$ (kg/mol) | $T_g$ (°C) | Polymerization method | Ref. |
|-----------|-------------------------|----------------|------------|----------------------|------|
| ![Phenol](image) | Phenol | 41 | 119 | RAFT | [53] |
| ![Guaiacol](image) | Guaiacol | 38 | 115-120 | RAFT | [25], [53] |
| ![Creosol](image) | Creosol | 34 | 121-132 | RAFT | [25], [53] |
| ![4-ethylguaiacol](image) | 4-ethylguaiacol | 35 | 108-116 | RAFT | [25], [53] |
| ![2,4-dimethoxyphenol](image) | 2,4-dimethoxyphenol | 23 | 111 | RAFT | [27] |
| ![2,3-dimethoxyphenol](image) | 2,3-dimethoxyphenol | 20 | 108 | RAFT | [27] |
| Compound               | RAFT/Free radical | Reference(s) |
|------------------------|-------------------|--------------|
| 3,5-dimethoxyphenol    | RAFT              | [27]         |
| Syringol               | RAFT              | [26], [27], [53] |
| Vanillin               | RAFT              | [25], [53]   |
| Syringaldehyde         | RAFT              | [53]         |
| Benzonitrile           | Free radical      | Present study|
| Vanillonitrile         | Free radical      | Present study|
| Syringonitrile         | Free radical      | Present study|