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

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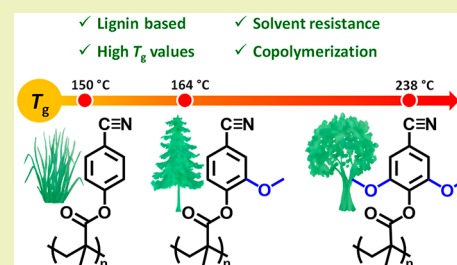
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Supporting Information

ABSTRACT: We here report on the synthesis and polymerization of nitrile-containing methacrylate monomers, prepared via straightforward nitrilation of the corresponding lignin-inspired aldehyde. The polymethacrylates reached exceptionally high glass transition temperatures (T_g values), i.e., 150, 164, and 238 °C for the 4-hydroxybenzonnitrile, vanillonitrile, and syringonitrile derivatives, respectively, and were thermally stable up to above 300 °C. Copolymerizations of the nitrile monomers with styrene and methyl methacrylate, respectively, gave potentially melt processable materials with tunable T_g values and enhanced solvent resistance. The use of lignin-derived nitrile-containing monomers represents an efficient strategy toward well-defined biobased high T_g polymer materials.

KEYWORDS: Vanillin, Syringaldehyde, Lignocellulose, Biobased plastics, Copolymers, Acrylate polymers, Glass transition temperature



INTRODUCTION

The development of new biobased thermoplastic polymers from sustainable feedstocks is essential when addressing the issues caused by fossil-based plastics.^{1–6} In order to compete with and replace fossil-based conventional plastics, biobased polymers must be produced from inexpensive and sustainable natural sources, have suitable thermal and mechanical properties, and be readily processable.⁷ This is perhaps especially difficult to achieve when it comes to amorphous thermoplastic polymers with high glass transition temperatures ($T_g > 100$ °C) because of the great challenge to produce this kind of material from biobased feedstocks.⁸ The T_g indicates the thermal transition between glassy (hard) and rubbery (soft) materials and is the most characteristic property of an amorphous polymer. Consequently, to a large degree, it determines the maximum use temperature and possible application areas.

The incorporation of aromatic or inflexible aliphatic ring structures to restrict the macromolecular chain mobility is a common and efficient strategy to increase the T_g and the thermal stability of polymers.⁹ Consequently, cyclic compounds like terpenes,^{8,10–13} vanillin,^{14,15} glucose,¹⁶ and isosorbide^{8,17,18} are common building blocks to prepare biobased high T_g polymers. The most abundant biosource of aromatic compounds is lignin, a byproduct of the paper and pulp industry. Lignins are biopolymers consisting of hydroxyphenyl, guaiacyl, and syringyl units, whose relative amounts depend on the natural source. (e.g., softwood or hardwood, Scheme 1).^{19–21} The depolymerization and purification of

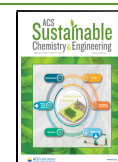
lignin remains however a challenge,^{19,22} thus only vanillin can nowadays be isolated from lignin in large scale (ca. 3000 tons/year).²³ A wide variety of lignin-based polymers have been prepared and studied in the past few years.^{8,14,15,24} For example, recently it was reported that softwood lignin-based polymethacrylates based on guaiacol, 4-ethylguaiacol, creosol, and vanillin, respectively, reached T_g values ranging from 111 to 129 °C, suitable for thermoplastic elastomer and binder applications.²⁵ These polymethacrylates, as well as similar ones based on phenol, syringol, and syringaldehyde, respectively, have been produced and investigated for various coating applications.^{26,27} Lignin-derived building blocks, such as eugenol,²⁸ have also been employed to produce densely cross-linked thermosets with high T_g values.

A far less exploited strategy to enhance and control the thermal properties of biobased polymers is to introduce strongly polar groups. The presence of these groups will increase the T_g by increasing intermolecular interactions but will also typically increase the thermal stability and enhance the solvent resistance. The nitrile group is highly polar and has been introduced into styrenic materials to improve both mechanical properties and chemical resistance. For example,

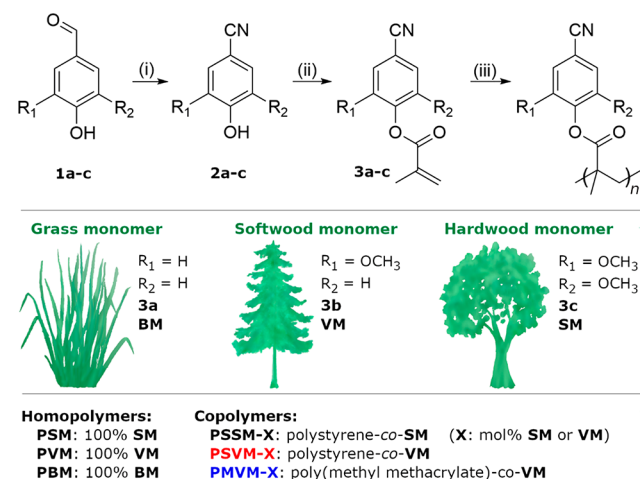
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Scheme 1. Synthetic Pathway, Nomenclature, and Molar Compositions of Lignin-Inspired Nitrile-Containing Methacrylate Monomers and Polymers^a



^aReagents and conditions: (i) hydroxylamine-*O*-sulfonic acid (1.1 equiv), acetic acid (1 equiv)/water, 50 °C, 6 h (yield 79%–82%); no column chromatography required; (ii) methacrylic anhydride (1.01 equiv), catalytic DMAP (2 mol %), ethyl acetate, 60 °C, 24 h (yield 70%–89%); (iii) AIBN (0.1–1 mol %), DMSO, 60 °C, 24 h.

poly(styrene-*co*-acrylonitrile) (SAN) has a T_g above 100 °C, depending on the acrylonitrile content.²⁹ Moreover, benzonitrile methacrylate polymers have recently been predicted by artificial neural network to possess high T_g .³⁰ From an industrial point of view, nitrilation is readily achieved by ammoxidation, using ammonia, oxygen, and a vanadium or molybdenum oxide catalyst.^{31,32} With the aim to develop biobased high-performance polymethacrylates with high T_g values resulting from both high macromolecular chain rigidity and polarity, we have in the present work prepared three different nitrile-containing methacrylate monomers. These monomers are based on lignin-inspired building blocks, namely, 4-hydroxybenzaldehyde **1a**, vanillin **1b**, and syringaldehyde **1c**, which correspond to hydroxyphenyl, guaiacyl, and syringyl lignin units, respectively.²⁰ (Scheme 1). The phenolic

rings of these building blocks are substituted with 0, 1, and 2 methoxy groups, respectively, and were selected to tune the chain rigidity. The monomers were employed in free-radical polymerizations, and the resulting homopolymers were characterized with respect to thermal properties and solvent resistance. Moreover, the nitrile-containing monomers were utilized in copolymerizations with styrene (S) and methyl methacrylate (MMA), respectively, to study their influence on the properties. The thermal stability and melt processability of the copolymers were subsequently investigated by rheology measurements.

RESULTS AND DISCUSSION

The monomers were synthesized in one or two steps according to Scheme 1. In step (i), the aldehyde groups of 4-hydroxybenzaldehyde and syringaldehyde first underwent nitrilation. This transformation has previously been carried out by various methods. Schuerch³³ reported the direct nitrilation of vanillin to vanillonitrile by the Schmidt reaction, using sodium azide as the nitrogen source. Lewis acids can also be used as catalysts as reported by Nimnual et al.³⁴ Recently, new chemoselective methods using triflic acid as a mediating agent have been reported.³⁵ In the present case, we used a greener approach developed by Quinn et al.³⁶ which involves the inexpensive hydroxylamine-*O*-sulfonic acid. This nitrogen source is less hazardous compared to azides.^{37,38} Moreover, the reaction conditions have a low environmental impact since the reaction is carried in an aqueous acetic acid solution. Thus, 4-hydroxybenzonitrile **2a** and syringonitrile **2c** were readily synthesized by this procedure with reasonably high yields, i.e., 82% and 79% for **2a** and **2c**, respectively (Scheme 1, SI). The products required no purification by chromatography, thus making this process easily scalable. Vanillonitrile **2b** was obtained directly from a commercial source. Alternatively, it is possible to produce **2b** from vanillin by green catalysis³⁹ or by directly converting the methyl group of 4-methylguaiacol through ammoxidation.^{31,40} The latter is of particular interest since ammoxidation is a conventional industrial process. Moreover, various other methylated aromatic compounds can be isolated from lignocellulose, thus making ammoxidation

Table 1. Polymerization and Thermal Data of the Different Benzonitrile-Containing Polymers

Sample name	Nitrile monomer feed (mol %)	Nitrile monomer content in polymer (mol %) ^a	Isolated yield (%) ^b	M_n (kg/mol)	\bar{D}	$T_{d(95\%)}^c$ (°C)	T_g^d (°C)
PBM	100	100	49	36 ^d	2.1 ^d	302	150
PVM	100	100	72	23 ^c /21 ^d	2.8 ^c /2.7 ^d	303	164
PSM	100	100	93	44 ^c /43 ^d	2.3 ^c /2.1 ^d	319	238
PSSM-16	10	16	80	19 ^c	1.8 ^c	317	123
PSSM-25	20	25	70	24 ^c	1.7 ^c	339	139
PSSM-35	30	35	91	21 ^c	1.6 ^c	324	152
PSSM-42	40	42	98	24 ^c	1.9 ^c	322	163
PSSM-50	50	50	89	30 ^c	1.8 ^c	330	173
PSVM-14	10	14	67	20 ^c	1.6 ^c	340	109
PSVM-28	20	28	72	26 ^c	1.7 ^c	341	123
PSVM-45	50	45	97	39 ^c	1.8 ^c	334	128
PMVM-18	10	18	93	85 ^c	1.9 ^c	261	128
PMVM-41	30	41	63	163 ^c	1.5 ^c	247	139

^aDetermined by ¹H NMR spectroscopy. ^bDetermined gravimetrically. ^cDetermined by SEC in THF. ^dDetermined by SEC in DMF. ^eDetermined by TGA at 5% weight loss under N₂.

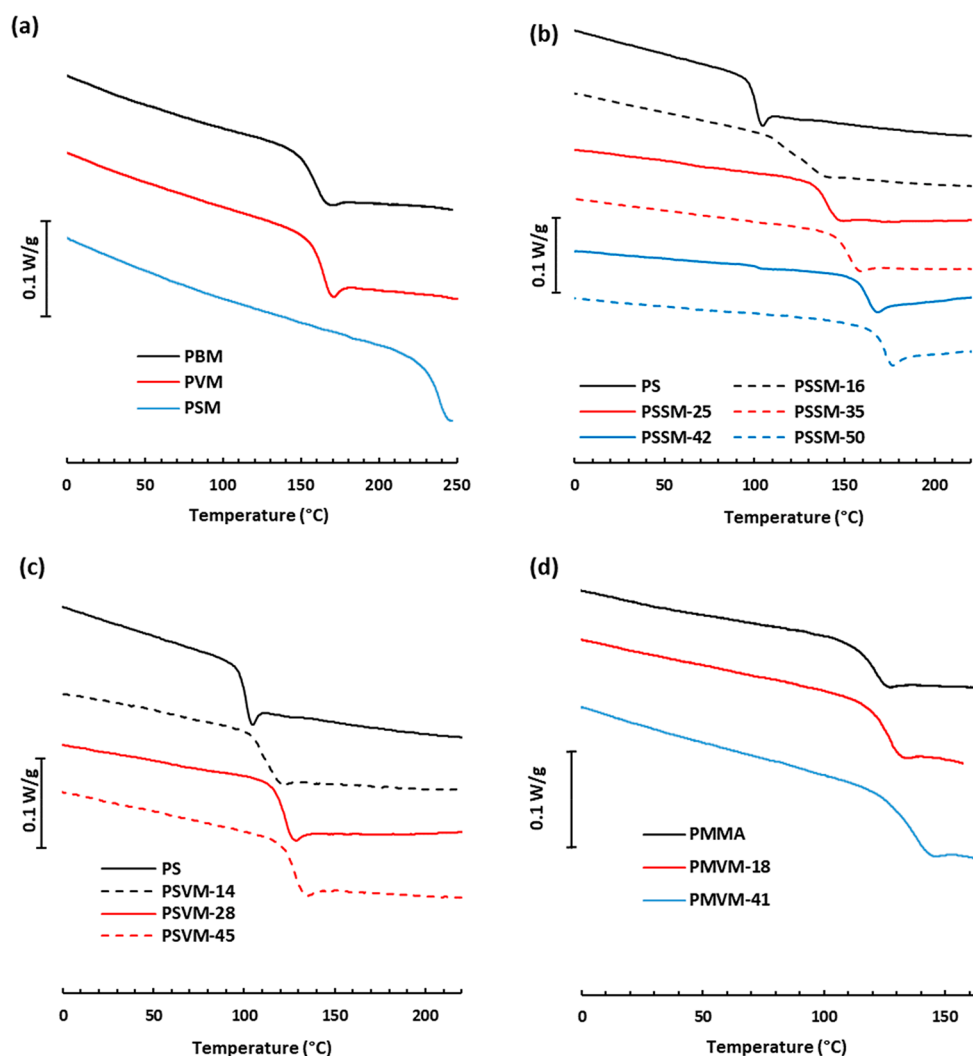


Figure 1. Second heating DSC traces of (a) homopolymers PBM, PVM, and PSM, (b) the PSSM series, (c) the PSVM series, and (d) the PMVM series under N_2 atmosphere at $10\text{ }^\circ\text{C min}^{-1}$.

an attractive reaction in the preparation of building blocks for high T_g biobased polymers.

In step (ii), 4-hydroxybenzoxonitrile **2a**, vanillonitrile **2b**, and syringonitrile **2c** were reacted with methacrylic anhydride in EtOAc using 4-(dimethylamino)pyridine (DMAP) as a catalyst.^{41,42} The products 4-hydroxybenzoxonitrile methacrylate **BM**, vanillonitrile methacrylate **VM**, and syringonitrile methacrylate **SM** were readily isolated by straightforward filtration and extraction. **SM** required further purification by aluminum oxide column chromatography to remove residual acid and phenol. The structures and purities of **BM**, **VM**, and **SM** (**3a-c**, respectively) were confirmed by ^1H NMR spectroscopy. All the signals from **2a** and **2c** were assigned according to literature.^{35,43} The signals from the **BM**, **VM**, and **SM** monomers were also assigned, and no signals from residual phenolic $-\text{OH}$ were detected. Today, methacrylic anhydride is produced from fossil sources, but sustainable pathways to methacrylic acid, and subsequently methacrylic anhydride, have been investigated. For example, biobased methacrylic acid has been prepared from both itaconic acid and citric acid^{44–47}

The **BM**, **VM**, and **SM** monomers were used to prepare the corresponding homopolymers by free radical polymerization, which is the dominating polymerization procedure employed by industry. The polymerizations were carried out in DMSO

solutions during 24 h by thermally initiated free radical polymerization using 2,2'-azobis(2-methylpropanitrile) (AIBN) as the initiator (Scheme 1). In general, toxicological assays of DMSO show low toxicity, and it is considered safe for pharmaceutical usage.⁴⁸ Still, it was recently reported that DMSO induces changes in cellular processes⁴⁹ and is therefore recommended to be substituted.^{50,51} To this extent, green solvents with solubility parameters close to that of DMSO (e.g., acetone, MEK, Cyrene⁵²) can be investigated as substitutes for DMSO. The corresponding homopolymers **PBM**, **PVM**, and **PSM** were isolated as white powders after precipitation in methanol, with 49%, 72%, and 93% yields, respectively (Table 1). The variation in the yield may result from differences in the solubility of these highly polar polymers during the polymerization, as the methoxy groups induced a higher solubility in DMSO. The polymerizations were confirmed by ^1H NMR spectroscopy by observing the disappearance of the alkene signals from the methacrylate moiety. Analysis by size-exclusion chromatography (SEC) showed that **PBM**, **PVM**, and **PSM** reached reasonably high number-average molecular weights (M_n), 36, 23, and 44 kg/mol, corresponding to a degree of polymerization (X_n) of 192, 106 and 178, respectively. The latter two samples were analyzed in both DMF and THF, while the former sample was

insoluble in THF and was analyzed only in DMF (Table 1). For both eluents, the calibration was performed using PEO standards. The chromatograms showed a bimodal distribution (Figure S10a) but also some tailing that could be due to interaction with the columns. This may explain the high \bar{D} values, 2.1, 2.8, and 2.3 for PBM, PVM, and PSM, respectively. Moreover, the solutions became slightly hazy during the polymerization, which indicated polymer aggregations and a partly heterogeneous polymerization, thus possibly limiting M_n and increasing \bar{D} . Also, we cannot exclude the possibility that the SEC analysis was influenced by interpolymer aggregation facilitated by interactions between the strongly polar nitrile groups. The most important use of the highly polar nitrile-containing monomers is not for the preparation of homopolymers but rather to incorporate smaller amounts into styrenic and acrylic materials to tune and enhance properties such as solvent resistance and shape retention.

Here, we studied the effect of the incorporation of the VM and SM monomers on the properties of polystyrene (PS) and poly(methyl methacrylate) (PMMA). Three series of copolymers were produced using similar conditions as for the homopolymerizations, and we chose to investigate the VM more extensively in these copolymerizations because of its higher accessibility. Thus, VM was copolymerized with S and MMA to form the PSVM and PMVM series, respectively (to simplify the acronyms, MMA was shortened to M). In addition, SM and S were copolymerized to produce the PSSM series (Scheme 1). In contrast to the homopolymerizations, the solutions remained optically clear throughout the copolymerizations. The copolymer contents were determined by ^1H NMR spectroscopy, and M_n and \bar{D} of the copolymers were determined by SEC (Table 1). A general trend showed that the molar fractions of the VM and SM monomers were higher in the copolymers than in the feeds, indicating a higher reactivity of these monomers compared to S and MMA in the copolymerizations. The copolymers in the PSSM series showed M_n between 19 and 30 kg/mol, and the PSVM series copolymers had M_n in the range 20 to 39 kg/mol, all with a markedly lower dispersity than the homopolymers ($1.6 < \bar{D} < 1.9$). The SEC curves of these copolymers showed a monomodal distribution (Figure S10b and c) which may result from the much higher solubility in DMSO compared with the homopolymers, due to their much lower nitrile content that reduces the intermolecular interactions. The M_n values were moderately high and seemed to increase with the VM or SM content, possibly reflecting the higher reactivity of these monomers compared to S. To increase M_n , the PMVM copolymers were produced at a higher monomer concentration. Consequently, the PMVM copolymers showed much higher molecular weights with $M_n = 85$ and 163 kg/mol, respectively; the SEC curve of PMVM-41 displayed a bimodal distribution despite showing a lower \bar{D} value (Figure S10d).

The thermal transitions of the polymers were characterized by differential scanning calorimetry (DSC) measurements. As expected, all the polymers were fully amorphous and displayed single glass transitions (Figure 1a). The T_g values measured for the homopolymers were 150, 164, and 238 °C for PBM, PVM, and PSM, respectively (Table 1). Consequently, T_g increased markedly with the number of methoxy groups present on the aromatic ring, which corroborates previous observations on methoxy-substituted polymethacrylates.^{9,53,54} The methoxy groups most probably prevent the rotation of the aromatic ring, thus reducing the segmental mobility of the polymer

chains. Notably, the opposite effect has been reported for vanillin-based epoxy networks, where the presence of a methoxy group on the aromatic ring resulted in a decreased T_g .⁵⁵ The present polymers show improved thermal properties compared to neat PS ($T_g = 100$ °C) and PMMA ($T_g = 105$ °C). Moreover, both PVM and PSM show significantly higher T_g values than corresponding non-nitrated polymers. Emerson et al. reported $T_g = 129$ and 201 °C for vanillin- and syringaldehyde-based polymethacrylates, respectively.⁵³ The higher T_g values of the present polymers can be explained by the very high polarity of the nitrile group in comparison to the aldehyde group ($\mu = 4.18$ and 2.77 D for benzonitrile and benzaldehyde, respectively).^{56,57} Hence, the nitrile-containing polymers reached significantly higher T_g values compared to other methoxy-substituted polymethacrylates (Table S2).^{25–27,53} The very high T_g values displayed by PVM and PSM motivated the study on the effect of the incorporating VM and SM into S and MMA copolymers. As expected, the DSC traces of the copolymers in the PSSM series presented gradually increasing values with the SM content, with $T_g = 100$, 123, and 173 °C for PS, PSSM-16, and PSSM-50, respectively (Figure 1b and Table 1). Similarly, the PSVM copolymers showed T_g values which gradually increased from 109 °C for PSVM-14 to 128 °C for PSVM-45 (Figure 1c and Table 1). Finally, the PMVM copolymers displayed T_g values which gradually increased from 121 to 128 and 139 °C for PMMA, PMVM-18, and PMVM-41, respectively (Figure 1d and Table 1). Hence, the T_g was observed to increase with the nitrile methacrylate content in all the copolymer series. Notably, the PMMA synthesized using the same protocol as the PMVM series showed a T_g of 121 °C, which was higher than the usually reported 105 °C for neat PMMA. As a matter of fact, PMMA obtained by free radical polymerization usually possess slightly syndiotactic-rich configuration ($rr \sim 60\text{--}70\%$), thus increasing T_g .⁵⁸ A ^1H NMR analysis of the present sample revealed a content of ca. 60% of rr triads, indicating a degree of syndiotacticity that can explain the higher T_g observed (Figure S6).

As shown in Figure 2, the variation of T_g with the VM and SM content, respectively, followed a linear trend for the PSSM, PSVM, and PMVM series in the form

$$T_g = T_g^0 + kf_{\text{CN}} \quad (1)$$

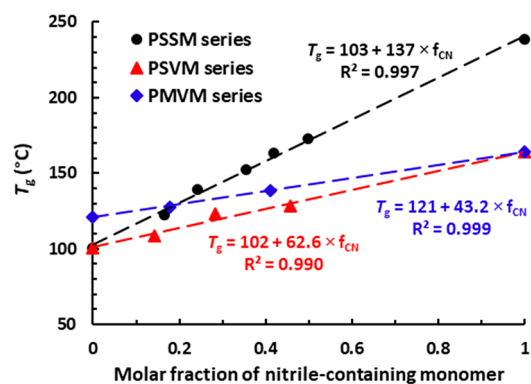


Figure 2. T_g of the homopolymers and copolymers versus the molar fraction of nitrile-containing monomer. The dashed lines indicate fittings to eq 1.

where f_{CN} is the molar fraction of the nitrile monomer. This indicates that the copolymers follow the rule of mixtures. In Figure S9, the variation of $1/T_g$ with the weight fraction of VM and SM, respectively, followed a linear trend for the PSSM, PSVM, and PMVM copolymer series, indicating that they also seemed to follow the Flory–Fox equation. In conclusion, the results showed that the T_g of styrenic and methacrylic materials can be tuned and enhanced in a controllable way by incorporating predetermined amounts of the biobased nitrile monomers. This is of particular interest for applications where, for example, high-temperature shape retention is required.

The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA) to study their thermal decomposition under N_2 atmosphere. The TGA traces showed that the PBM, PVM, and PSM homopolymers decomposed in one step at $T_{\text{d},95\%} = 302, 303, \text{ and } 319\text{ }^\circ\text{C}$, respectively (Figures S7a and S8a, Table 1). $T_{\text{d},95\%}$ seemed to increase with the number of methoxy groups on the aromatic ring, which might be explained by the increasing T_g (i.e., higher melt viscosity) of the polymers. Both PVM and PSM showed considerably higher $T_{\text{d},95\%}$ values than the corresponding non-nitrated vanillin- and syringaldehyde-based polymethacrylates reported by Holmberg and co-workers with $T_{\text{d},95\%} = 264 \text{ and } 303\text{ }^\circ\text{C}$, respectively.^{26,59} This demonstrated that the introduction of the nitrile group significantly enhanced the thermal stability. Furthermore, the $T_{\text{d},95\%}$ value reached to approximately 150 and $\sim 140\text{ }^\circ\text{C}$ above T_g for PBM and PVM, respectively, and to about $80\text{ }^\circ\text{C}$ above the T_g of PSM. This implied that the thermal window of PBM and PVM is sufficiently high to enable melt processing, which is generally performed ca. $30\text{--}70\text{ }^\circ\text{C}$ above the T_g of amorphous polymers. The narrower window of PSM indicated that the melt processing of this polymer is more restricted. The TGA traces of the copolymers are reported in Figure S7b–d. Here, $T_{\text{d},95\%}$ varied in the quite narrow range between $317 \text{ and } 330\text{ }^\circ\text{C}$ for the PSSM copolymers, $334 \text{ and } 341\text{ }^\circ\text{C}$ for the PSVM copolymers, and $247 \text{ and } 261\text{ }^\circ\text{C}$ for the PMVM copolymers (Table 1). No obvious trend between copolymer compositions and $T_{\text{d},95\%}$ was identified. For all the copolymers, the difference between $T_{\text{d},95\%}$ and T_g values was higher than $100\text{ }^\circ\text{C}$, which indicated that the copolymers may be melt processable.

Dynamic melt rheology was carried out in order to further investigate the processability of the copolymers. Thus, sample PSVM-14 was kept at $150\text{ }^\circ\text{C}$ during 20 min under a sinusoidal stress. As can be seen in Figure 3, $|\eta^*|$ and $|\dot{\gamma}^*|$ remained

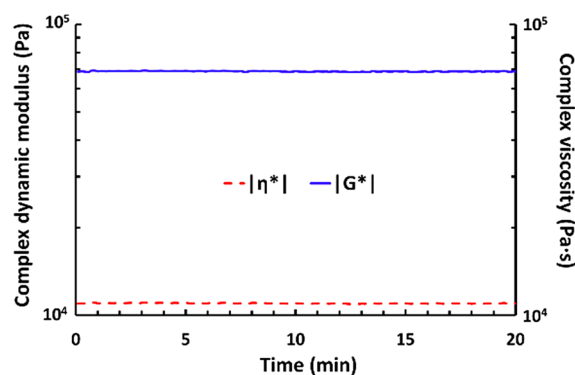


Figure 3. Dynamic melt rheology data of the complex dynamic shear modulus $|G^*|$ and complex viscosity $|\eta^*|$ for copolymer PSVM-14 at $150\text{ }^\circ\text{C}$ during 20 min at 0.1% strain.

constant throughout the experiment, which hinted that the sample did not suffer from any significant chain scission or cross-linking reactions and, hence, that PSVM-14 was stable under these conditions. This showed that the VM moiety did not degrade when exposed to a typical melt processing time and temperature, implying that the VM copolymers are melt processable.

The solvent resistance of the different polymers was probed by investigating the solubility in a wide range of solvents (Table S1) chosen according to their solubility parameter (δ), as well as their hydrogen bonding capacity. The highly polar nitrile-containing homopolymers were insoluble in strongly hydrogen-bonding solvents such as H_2O , MeOH, and 1-BuOH. They were soluble in DMSO but insoluble in Et_2O and toluene. As expected, PS was fully soluble in these latter two solvents, but the copolymers in the PSVM and PSSM series became nonsoluble in Et_2O and toluene as the nitrile-containing methacrylate content increased. Thus, PSVM-14 and PSSM-16 were insoluble in Et_2O , while PSVM-45 and PSSM-25 were insoluble in toluene. The introduction of VM and SM thus gave styrenic materials with solvent resistance characteristics comparable to SAN.⁶⁰ While PMMA was soluble in acetonitrile (ACN), PVM was not. Thus, the copolymers in the PMVM series became nonsoluble in ACN (as observed for PMVM-41). Consequently, both the VM and the SM monomers allowed efficient tuning of the solvent resistance of styrenic and acrylic polymer materials.

CONCLUSION

In summary, nitrile-containing methacrylates were readily prepared by nitrilation of corresponding lignin-inspired aldehyde-functional building blocks such as vanillin and syringaldehyde using environmentally benign methods, followed by methacrylation. The presence of the highly polar nitrile group and methoxy groups on the phenolic ring contribute to the exceptionally high T_g reached by the corresponding polymethacrylates. Copolymerizations to incorporate the monomers into styrenics and acrylics gave materials with enhanced and controllable T_g values and solvent resistance. In addition, thermal and rheological characterizations indicated that polymers containing vanillonitrile methacrylate were melt processable. The use of the lignin-inspired nitrile-containing methacrylates represents a new strategy to prepare high-performance biobased polymer materials with high dimensional stability and solvent resistance. Especially, vanillonitrile methacrylate holds great promise for applications within, for example, packaging, coating, and high-performance plastics applications because of the accessibility and potentially low cost of vanillin.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c07048>.

Experimental section containing description of materials and instruments (^1H NMR, SEC, TGA, DSC, rheology) and detailed experimental descriptions of all reported precursors, monomers, polymers and copolymers; ^1H NMR spectra of 2c, BM, VM, SM, PSSM-16, and PMMA; TGA data of the homopolymers and copolymers; Fox–Flory plot of the copolymers; SEC chromatograms of the homopolymers and copolymers;

solubility data of the homopolymers and copolymers; table with structures and T_g of reported lignin-based polymethacrylates (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

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

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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 F₂₅₄), 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 ($\varnothing = 15$ mm). Discs of PSVM-14, PSVM-28, PSSM-25 and PMVM-18 ($\varnothing = 15$ 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-Hydroxybenzoxitrile 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: *T*_m = 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: *T*_m = 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-*d*₆) 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-*d*₆) 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-d₆) 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-d₆) 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, CDCl₃) 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, CDCl₃) 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 (syronitrile methacrylate) SM 3c

To a 100 mL round-bottom flask equipped with a magnetic stirrer, 4-hydroxy-3,5-dimethoxybenzotrile **2c** (2.862 g, 15.97 mmol, 1.0 equiv.) and DMAP (39.4 mg, 0.323 mmol, 0.02 equiv.) were dissolved in EtOAc (26 mL). The flask was sealed and purged with vacuum/N₂ cycles. 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, CHCl₃) δ, ppm: 2.06 (m, 3H), 3.83 (s, 6H), 5.78 (m, 1H), 6.37 (m, 1H), 6.89 (s, 2H), ¹³C NMR (100.62 MHz, CDCl₃) δ, ppm: 18.5, 56.6, 109.1, 109.9, 118.7, 128.1, 133.1, 135.0, 153.0, 164.5; melting temperature: decomposition before reaching melting

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

In a schlenk flask, 10 mL of acetonitrile were degassed with vacuum/N₂ 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 acetone (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/N₂ 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/N₂ 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%).

NMR Spectra

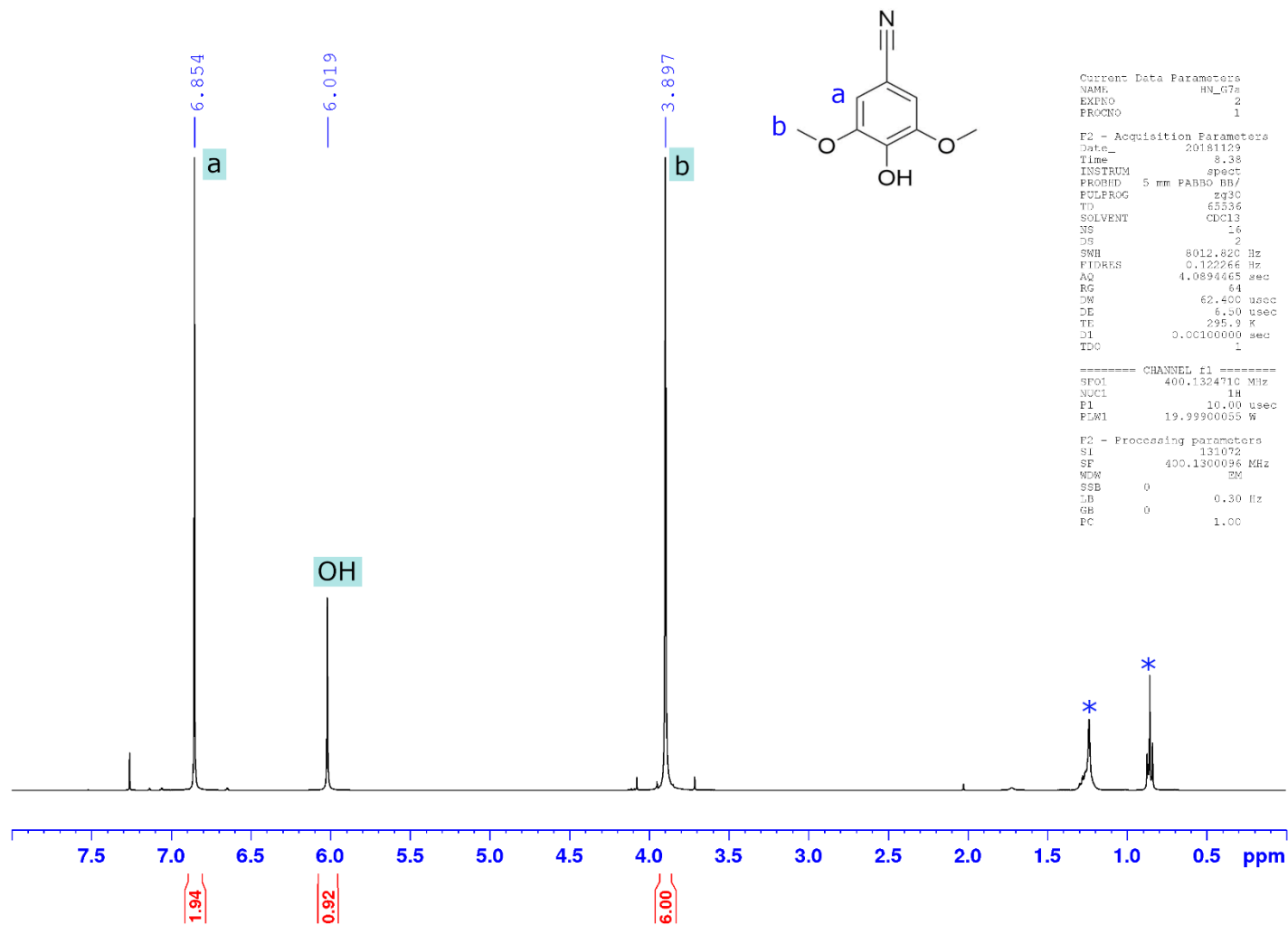


Figure S1. ^1H NMR spectrum of 4-hydroxy-3,5-dimethoxybenzonitrile (syringonitrile) **2c** (*indicates heptane signals).

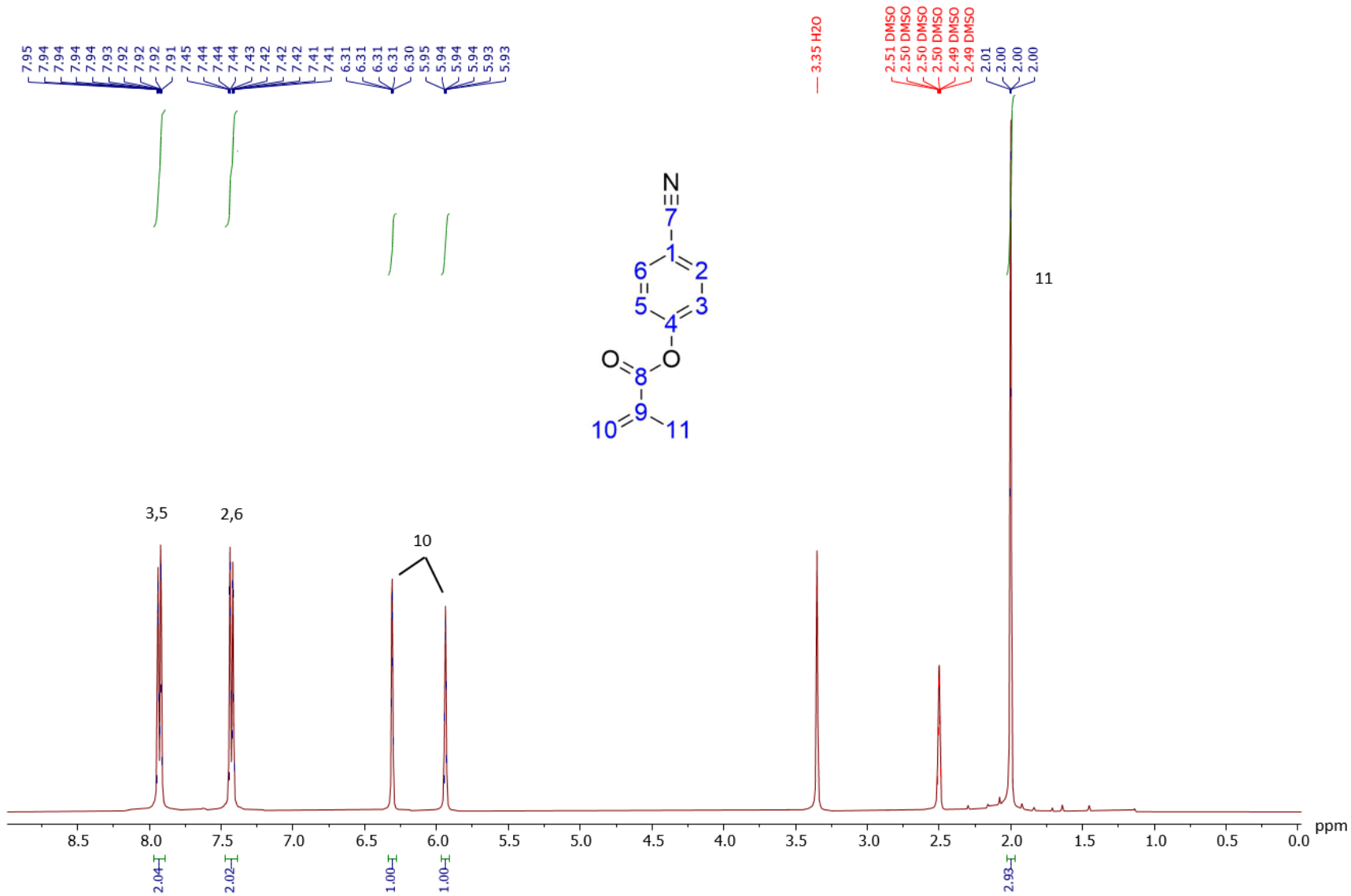


Figure S2. ¹H NMR spectrum of 4-cyanophenyl methacrylate (4-hydroxybenzonitrile methacrylate) **BM**.

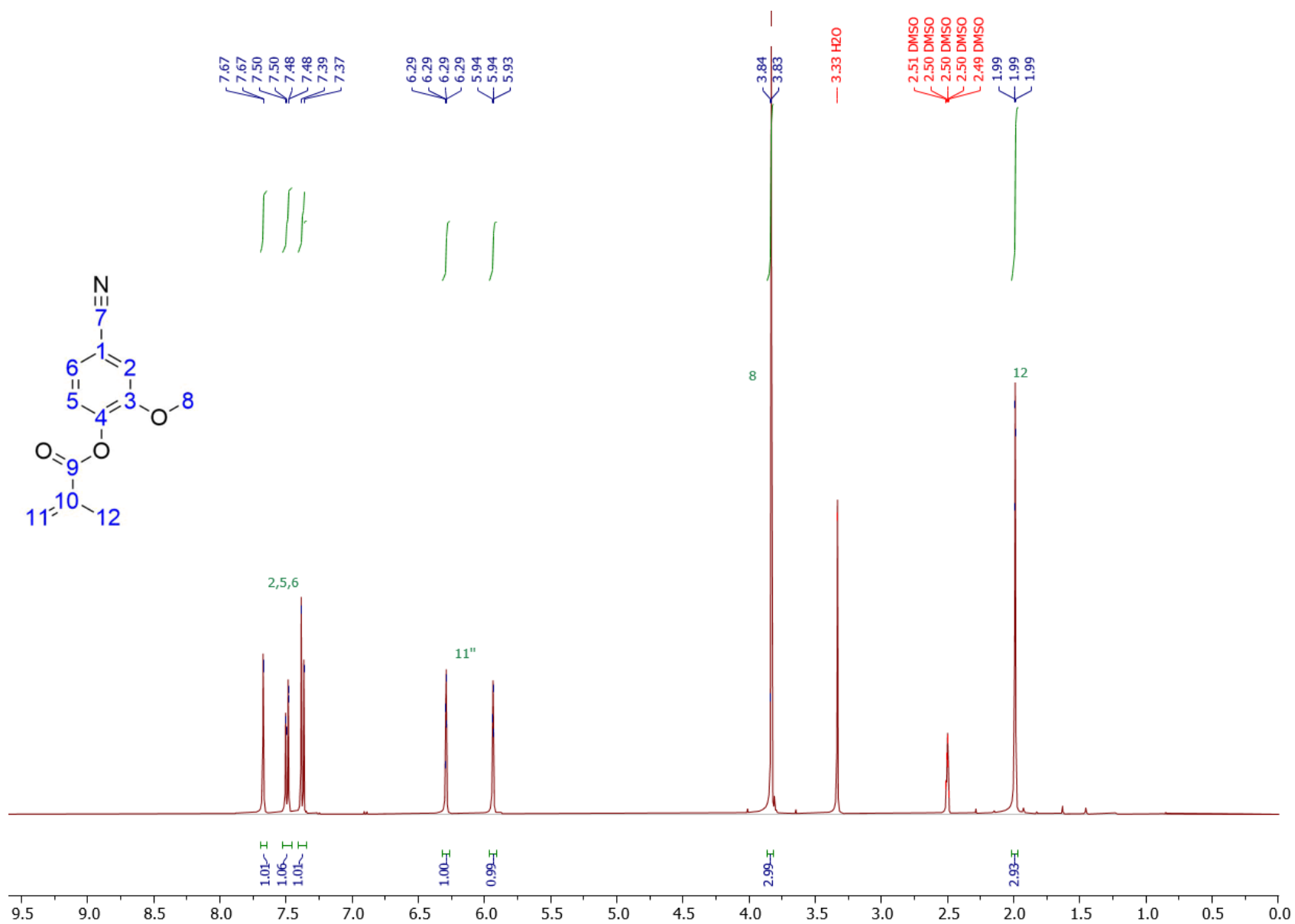


Figure S3. ¹H NMR spectrum of 4-cyano-2-methoxyphenyl methacrylate (vanillonitrile methacrylate) VM.

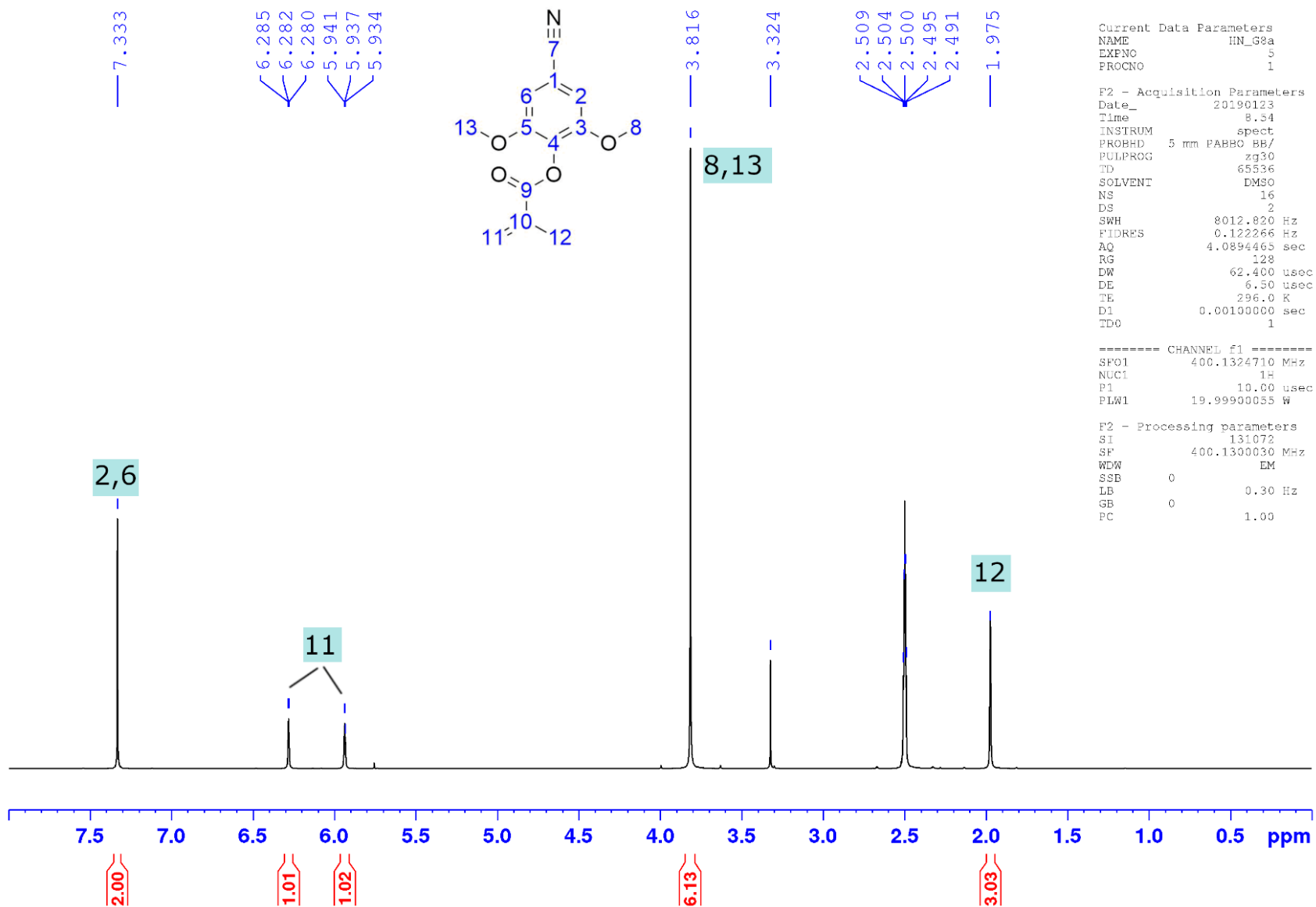


Figure S4. ¹H NMR spectrum of 4-cyano-2,5-dimethoxyphenyl methacrylate (syringonitrile methacrylate) SM.

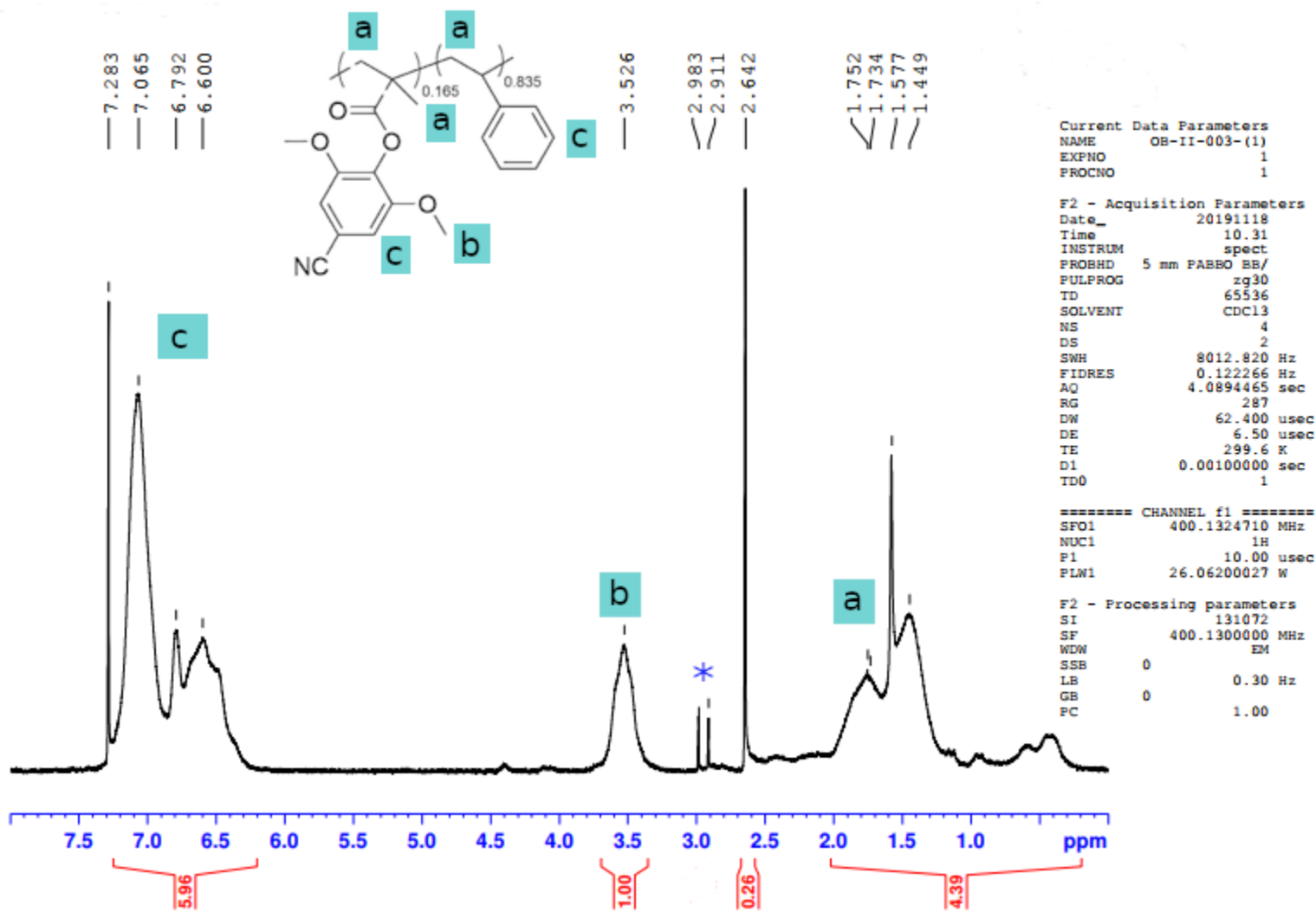


Figure S5. ^1H NMR spectrum of poly[styrene-*co*-(4-cyano-2,6-dimethoxyphenyl methacrylate)] PSSM-16. Signals **b** and **c** were used to determine the molar composition of the copolymers (*indicates DMF signals).

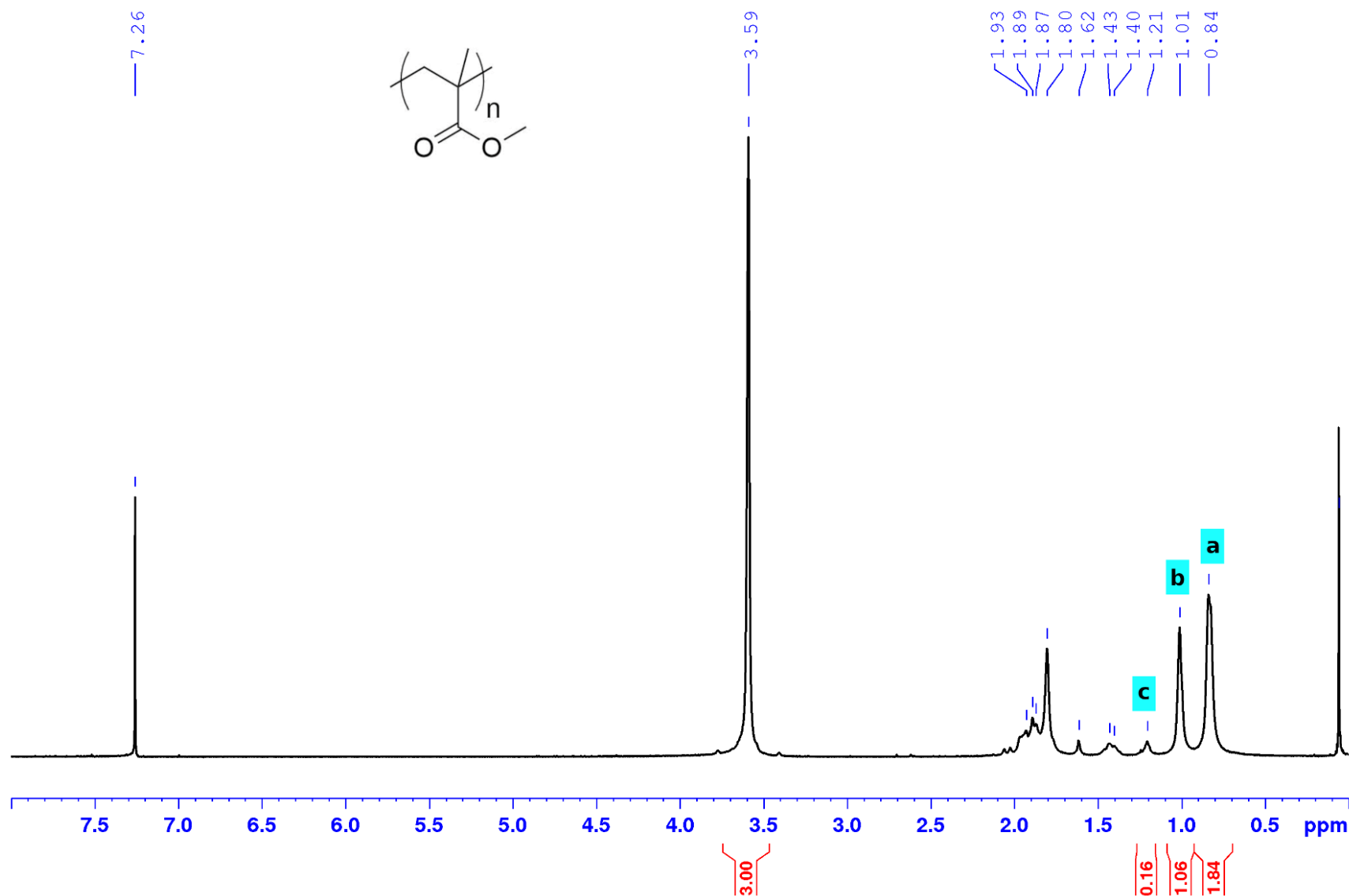


Figure S6. ¹H NMR spectrum of poly(methyl methacrylate) synthesized using the same procedure as the PMVM series. Signals **a**, **b** and **c** were used to determine the *rr*, *rm* and *mm* triad fractions, respectively.

TGA Traces

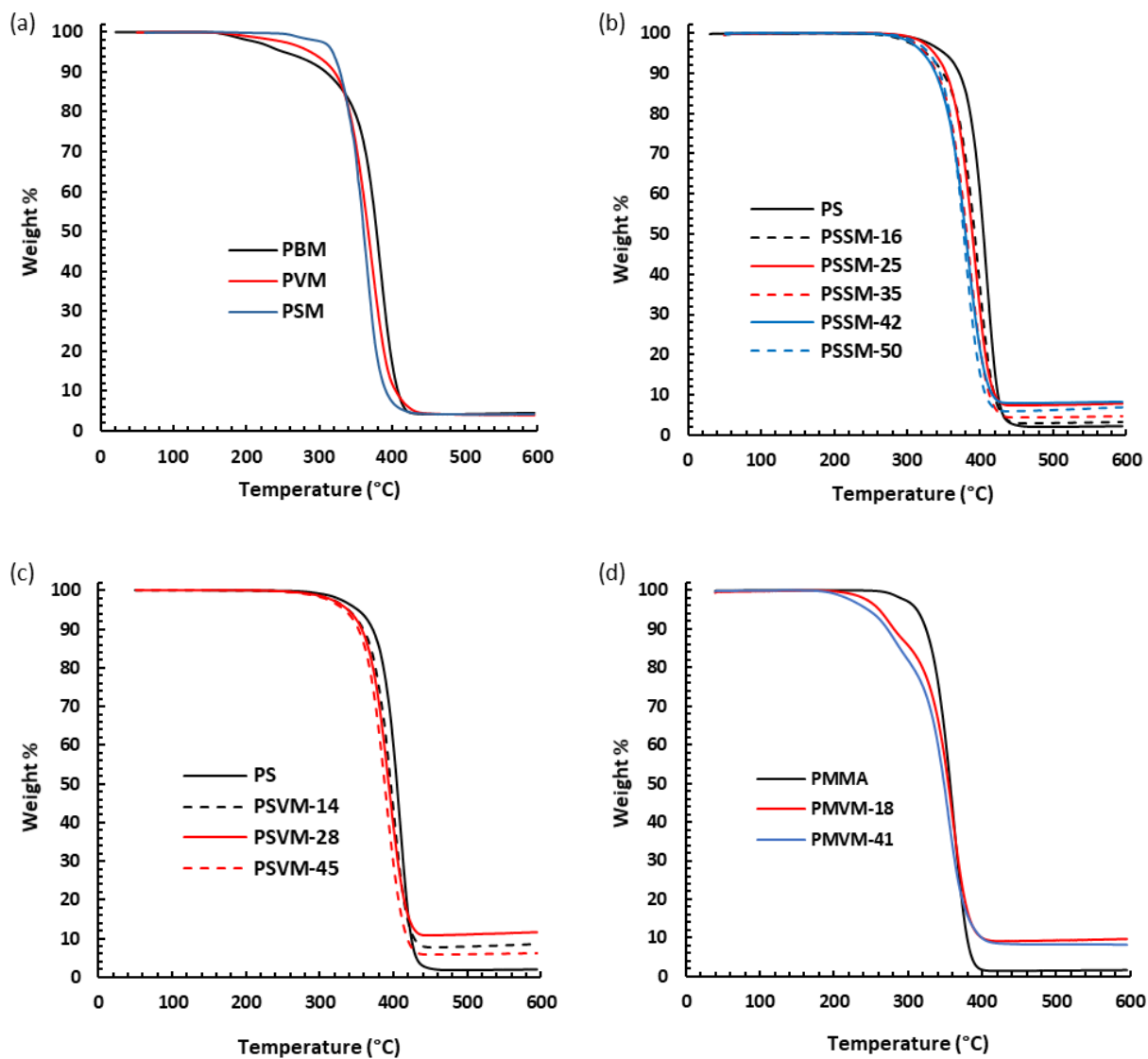


Figure S7. TGA traces of: (a) homopolymer PBM, PVM and PSM, (b) the PSSM series, (c) the PSVM series, and (d) the PMVM series under N₂ atmosphere at 10 °C min⁻¹.

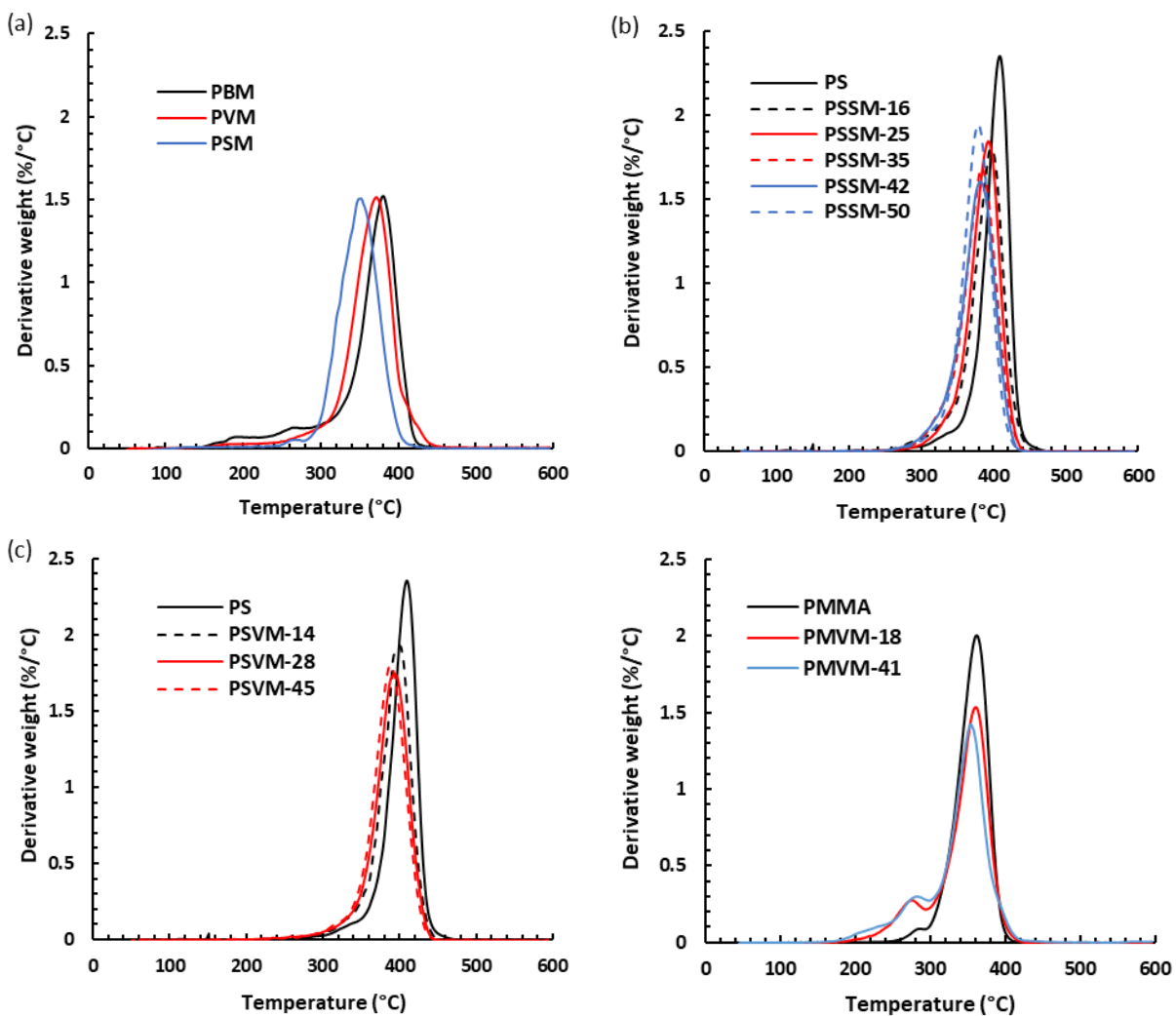


Figure S8. TGA derivative traces of: (a) homopolymer **PBM**, **PVM** and **PSM**, (b) the **PSSM** series, (c) the **PSVM** series, and (d) the **PMVM** series under N_2 atmosphere at $10\text{ }^\circ\text{C min}^{-1}$.

Flory-Fox plot

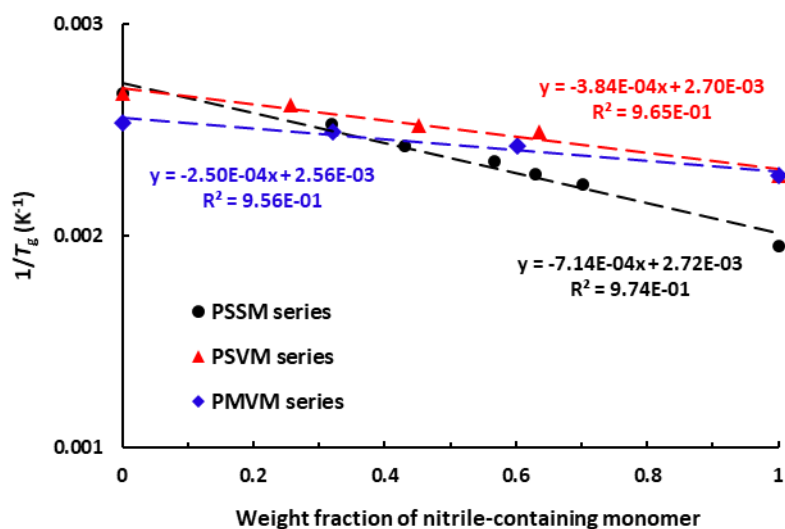
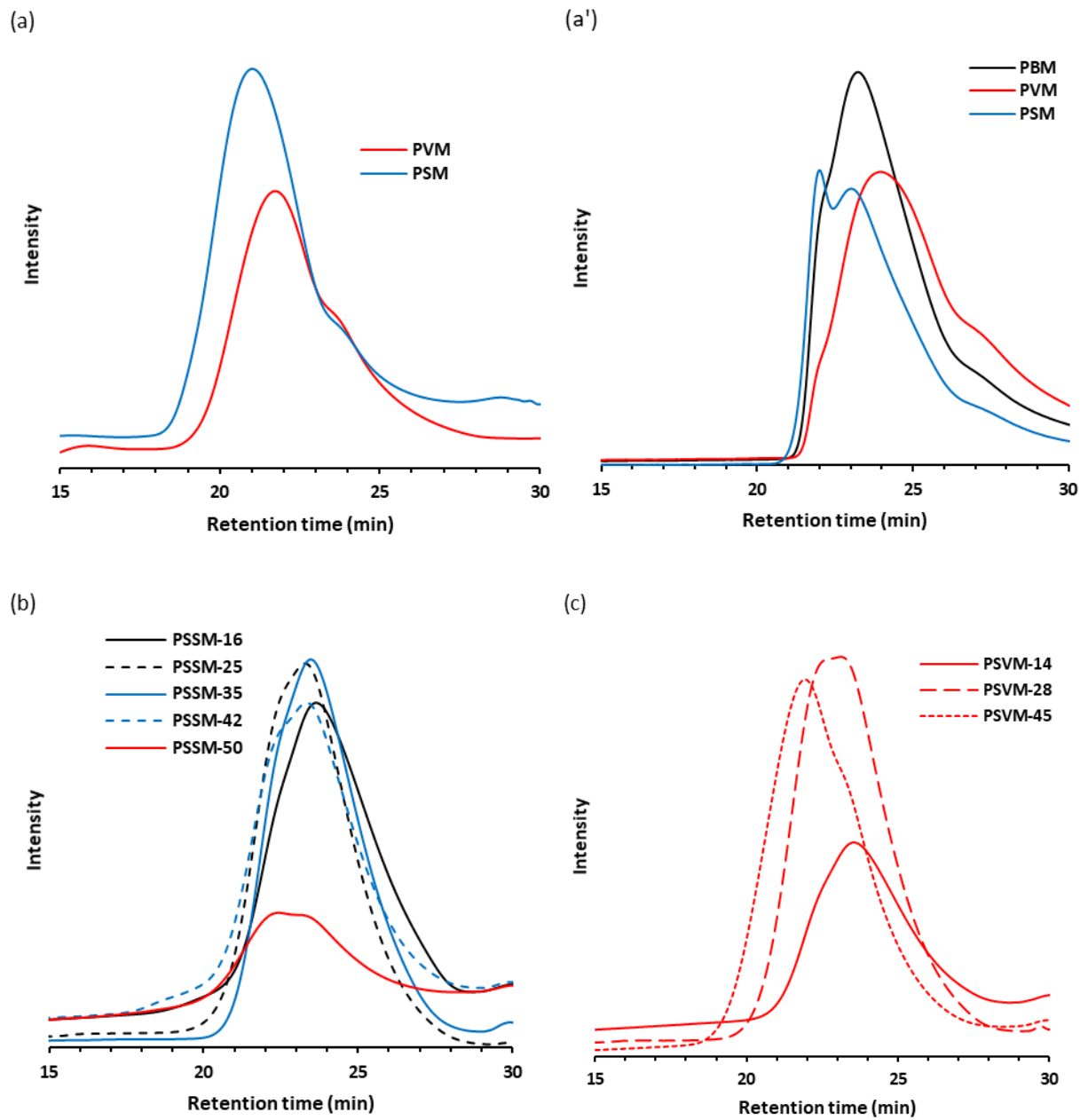


Figure S9. $1/T_g$ of the homopolymers and copolymers versus the weight fraction of nitrile-containing monomer. The fitted linear equations $y = ax + b$ are shown as dashed lines, where $a = 1/T_g(1) - 1/T_g(2)$ and $b = 1/T_g(2)$, with (1) referring to the nitrile containing polymer and (2) to PS or 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).



(d)

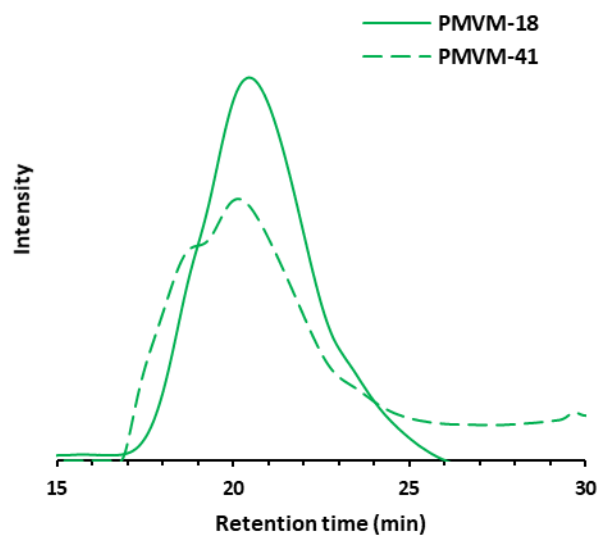


Figure S10. SEC of THF solutions of: (a) homopolymer **PVM** and **PSM**, (b) the **PSSM** series, (c) the **PSVM** series and (d) the **PMVM** series. “Intensity” is the differential refractive index (dRI) of the RI detector in arbitrary units. SEC in DMF of (a’) homopolymers **PBM**, **PVM** and **PSM**.

Evaluation of the Solubility of Polybenzotrile methacrylates

The solubility of the different polybenzotrile 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.

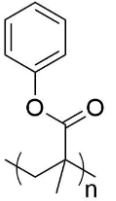
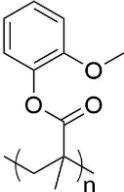
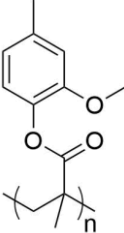
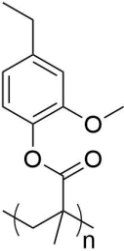
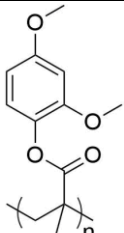
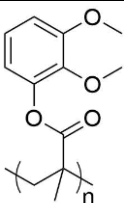
Table S1. Solubility of the nitrile-containing polymers at 21 °C.

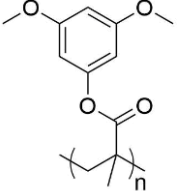
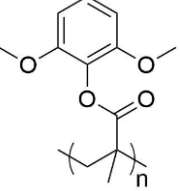
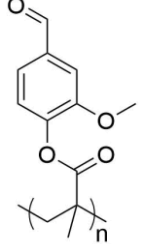
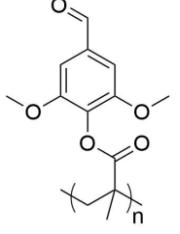
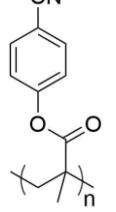
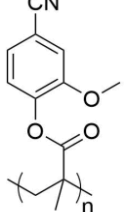
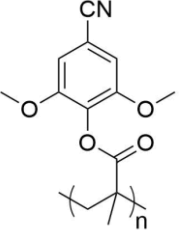
Polymer	Solvent ^a								
	H ₂ O $\delta=48$ (s)	MeOH $\delta=43$ (s)	1-BuOH $\delta=23$ (s)	DMSO $\delta=25$ (m)	THF $\delta=19$ (m)	Et ₂ O $\delta=15$ (m)	ACN $\delta=24$ (p)	CHCl ₃ $\delta=19$ (p)	Toluene $\delta=18$ (p)
PS	-	-	-	-	+	+	-	+	+
PBM	-	-	-	+	-	-	-	-	-
PSVM-14	-	-	-	-	+	-	-	+	+
PSVM-28	-	-	-	+	+	-	-	+	+
PSVM-45	-	-	-	+	+	-	-	+	-
PVM	-	-	-	+	+	-	-	-	-
PSSM-16	-	-	-	-	+	-	-	+	+
PSSM-25	-	-	-	+	+	-	-	+	-
PSSM-35	-	-	-	+	+	-	-	+	-
PSSM-42	-	-	-	+	+	-	-	+	-
PSSM-50	-	-	-	+	+	-	-	+	-
PSM	-	-	-	+	+	-	+	+	-
PMMA	-	-	-	+	+	-	+	+	+
PMVM-18	-	-	-	-	+	-	+	+	+
PMVM-41	-	-	-	-	+	-	-	+	+

^aThe symbols “+” and “-” indicate solubility and nonsolubility, respectively. Solubility parameters (δ , MPa^{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	41	119	RAFT	[53]
	Guaiacol	38	115-120	RAFT	[25], [53]
	Creosol	34	121-132	RAFT	[25], [53]
	4-ethylguaiacol	35	108-116	RAFT	[25], [53]
	2,4-dimethoxyphenol	23	111	RAFT	[27]
	2,3-dimethoxyphenol	20	108	RAFT	[27]

	3,5-dimethoxyphenol	23	82	RAFT	[27]
	Syringol	24	203-205	RAFT	[26], [27], [53]
	Vanillin	36	129-139	RAFT	[25], [53]
	Syringaldehyde	29	201	RAFT	[53]
	Benzonitrile	36	150	Free radical	Present study
	Vanillonitrile	23	164	Free radical	Present study
	Syringonitrile	44	238	Free radical	Present study