Supporting information

Thermotropic polyesters from 2,5-furandicarboxylic acid and vanillic acid: Synthesis, thermal properties, melt-behavior, and mechanical performance

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Molecular weight build-up and reaction time.

During the synthesis of these polyesters, we observed that the time required to build up molecular weight increases with the increasing amounts of vanillic acid and/or 2,5-FDCA. To probe this behavior, polymerizations were performed at 230 °C and samples were taken over time during the polycondensation step performed under reduced pressure. Figure S1 shows the molecular weight build-up over time for polymers containing BP as the diol. It can be seen that the molecular weight build-up for polymer **3b** (having no FDCA and/or VA) is rather slow and levels off rapidly, which is due to solidification of the reaction mixture after 120 minutes. The addition of 10 mole% VA (**4e**) lowers the melting temperature, prevents the solidification of the reaction mixture, and allows for more extensive build-up of molecular weight. A number-average molecular weight (M_n) in excess of 20,000 g/mol is obtained within two hours of reaction under reduced pressure. Interestingly, the copolymerization of 25 mole% of VA (**4f**) proceeds much slower and a M_n of roughly 15,000 g/mol is obtained after seven hours of the reaction time. A similar increase in the reaction time was observed during the synthesis of polymer **4d**, which required over six hours of synthesis under reduced pressure to obtain a M_n of 12,800 g/mol. For comparison, the application of two hours of reduced pressure during the synthesis of polymer **3a** resulted in a molecular weight of 24,800 g/mol. For this reason, it is expected that the presence of the bulky methoxy group next to the acetic acid ester bond in the acetylated VA sterically hinders the ester exchange reaction occurring during polymerization. The slower incorporation of the VA monomer therefore requires increased reaction times to obtain a higher molecular weight.

The reaction time required to build up molecular weight increased even further for systems containing both 2,5-FDCA and VA. For example, more than 10 hours were needed to build up a

M_n of 12,000 g/mol during synthesis of the polymer **5b**. Recent studies showed that 2,5-FDCA exhibits a poor dissolution behavior in the monomer/oligomers mixture at these reaction temperatures.[i] It is expected that the slow reaction rate of VA and the slow dissolution of 2,5-FDCA are responsible for the increased reaction times required to build up molecular weight. Furthermore, these increased reaction times resulted in slow sublimation of 2,5-FDCA and hampered the molecular weight build-up even further due to the generated stoichiometric imbalance.
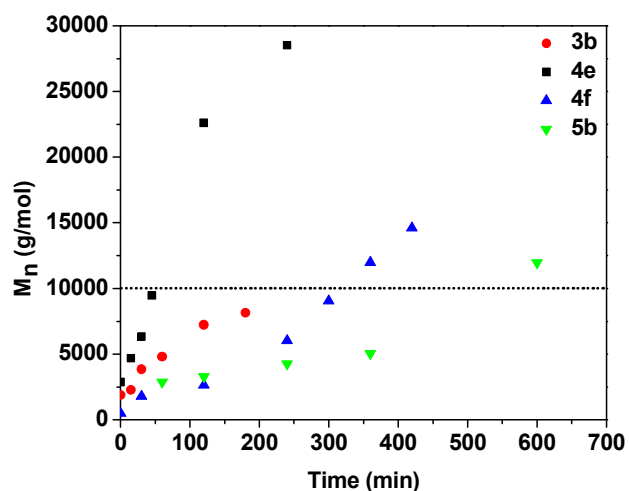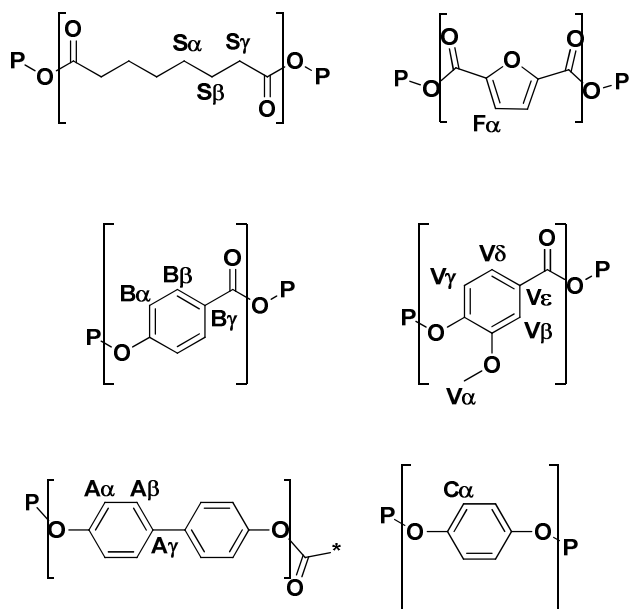

Figure S1. Number-average molecular weight build-up over time for systems containing BP with varying amounts of VA and 2,5-FDCA.

Variable temperature solid-state ^{13}C{^{1}H} CP/MAS and INEPT MAS NMR

Temperature-dependent solid-state NMR ^{13}C{^{1}H} CP/MAS and ^{13}C{^{1}H} INEPT MAS NMR measurements have been performed to follow the molecular changes during heating of polymers **3a**, **4c**, **4d** and **5b**. Scheme S1 shows the structural formulas of the monomer residues present in these polymers and the labels of the corresponding carbon atoms. Figure S2 shows the overlay of the ^{13}C{^{1}H} CP/MAS and ^{13}C{^{1}H} INEPT MAS NMR measurements taken over temperature for polymer **3a** in the region between 140 and 0 ppm. Below the glass transition temperature of the polymer (<35 °C), broad peaks are observed in the ^{13}C{^{1}H} CP/MAS NMR spectrum (Figure S1a) with moderate intensity, indicating that the polymer chains reside in a rigid amorphous or crystalline phase. Upon heating to temperatures above T_g, the ^{13}C resonances assigned to **S$_α$, S$_β$, S$_γ$, B$_α$, B$_β$,** and **C$_α$** become sharper and the signal intensities increase due to more favorable CP conditions. Interestingly, no significant change of the carbons close to the carbonyls (**B$_γ$**) is observed. This suggests that the motion of the aromatic moieties is restricted to the rotation of the phenyl rings (not shown). Heating of the polymer above the onset of melting leads to a further sharpening of the peaks, while **B$_γ$** decreases in intensity (>150 °C) as can be seen in Figure S2a. The increased intensity of the ^{13}C signals in the molten phase can be explained by the high mobility of the phenyl rings and aliphatic carbons in the oriented nematic phase. The effective T_2 relaxation time of these carbons and protons increases upon melting and signals start to rise in the ^{13}C{^{1}H} INEPT MAS NMR spectra shown in Figure S2b at 150 °C and higher. Upon further heating the intensity of the ^{13}C{^{1}H} INEPT MAS NMR spectra increases, indicating that a larger fraction of the polymer resides in the mobile liquid crystalline phase.

Scheme S1. Labels of the carbon atoms in the structural formulas of monomer residues present in polymer **3a.**
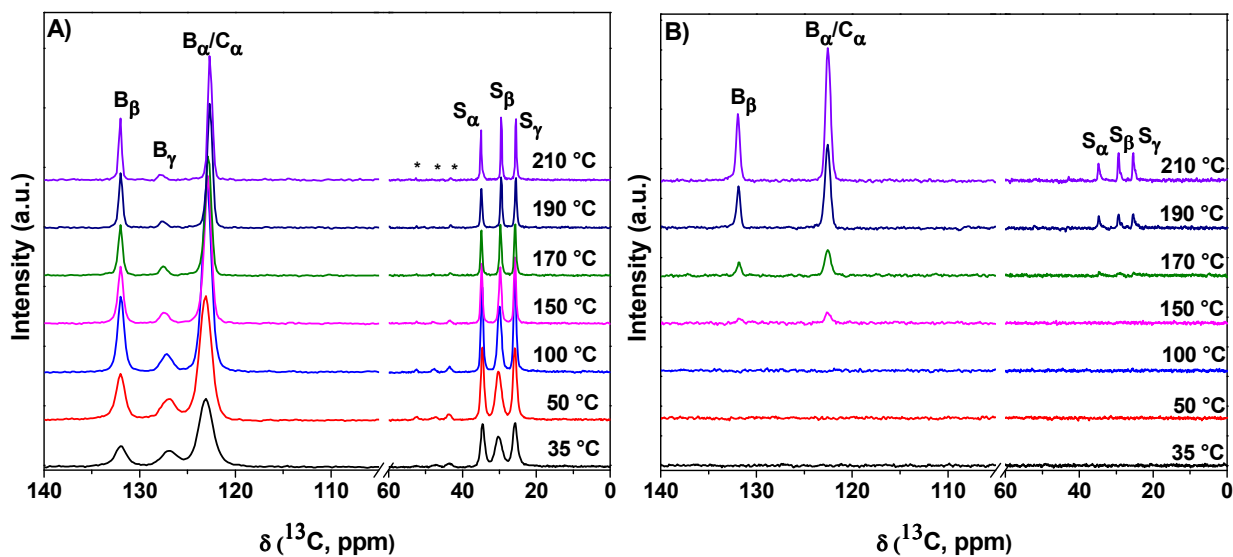

Figure S2: Temperature-dependent solid-state $^{13}C\{^{1}H\}$ CP/MAS NMR (**A**) and $^{13}C\{^{1}H\}$ INEPT MAS NMR (**B**) results obtained for sample **3a** in the region between 140 and 0 ppm. Signals denoted with an * are spinning sidebands. All experiments were recorded at 11.75 T (500.13 MHz for ^{1}H) using a MAS frequency of 10.0 kHz and ^{1}H decoupling during acquisition.

Figure S3 shows the ^{13}C{^{1}H} CP/MAS and ^{13}C{^{1}H} INEPT MAS NMR spectra of polymer **4c**, which shows the same signal sharpening above T_g (< 80 °C) as observed for polymer **3a** (see Figure S1). An increase in the flexibility of the phenyl rings and aliphatic spacers is clearly visible above T_g in the ^{13}C{^{1}H} CP/MAS NMR spectra indicated by the sharpening and increase of the ^{13}C signals (Figure S3a). The onset of melting is observed above 150 °C, which can be identified by the rise in resonance signals in the ^{13}C{^{1}H} INEPT MAS NMR spectra. Interestingly, the ^{13}C{^{1}H} CP/MAS NMR spectra obtained above 170 °C show the rise of a peak at 120.7 ppm, corresponding to the aromatic carbons (**F$_\alpha$**) of the 2,5-FDCA-moiety. The **F$_\alpha$** resonance is also visible in the ^{13}C{^{1}H} INEPT MAS NMR experiments above 190 °C, indicating a fraction of the 2,5-FDCA moieties becomes mobile at much higher temperatures than the other aromatic rings (Figure S3b). Moreover, we anticipate that the 2,5-FDCA moiety is unable to perform full rotations at temperatures below 190 °C due to the dipole moment that is induced upon rotation of the furan ring. For this reason it is expected that a higher thermal energy is required for the furan ring to rotate, compared to phenyl rings of HBA and HQ. Another possibility is that the mobile fraction observed at temperatures between 150 °C and 190 °C corresponds to the melting of crystals containing flexible chains. As observed by GPC and DSC analysis, polymer **4c** is of a blocky nature and crystals with high melting temperatures are expected to contain higher amounts of aromatic 2,5-FDCA than flexible suberic acid. Melting of these crystals requires a higher temperature compared to the melting of crystals containing the more flexible suberic acid, thus requiring higher temperatures to for the **F$_\alpha$** signal to become visible.
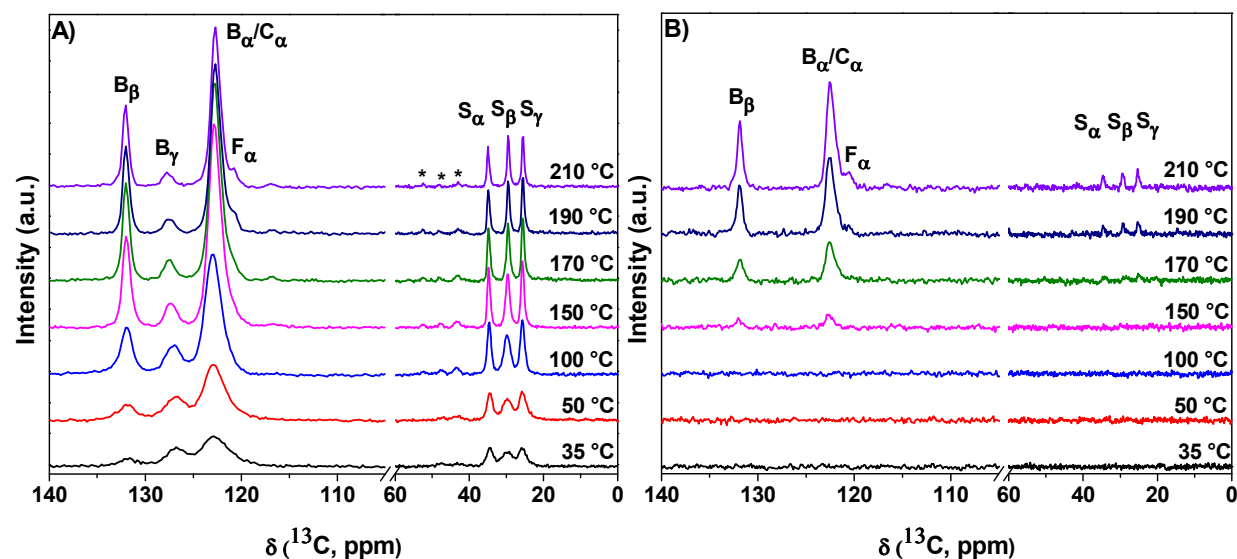
Figure S3: Temperature-dependent solid-state $^{13}C\{^{1}H\}$ CP/MAS NMR (**A**) and $^{13}C\{^{1}H\}$ INEPT MAS NMR (**B**) results obtained for sample **4c**. Signals are assigned according to Scheme S1 while the asterisks denote spinning sidebands. All experiments were recorded at 11.75 T (500.13 MHz for ^{1}H) using a MAS frequency of 10.0 kHz and ^{1}H decoupling during acquisition.

Figure S4 shows the temperature-dependent solid-state $^{13}C\{^{1}H\}$ CP/MAS and $^{13}C\{^{1}H\}$ INEPT MAS NMR spectra for polymer **4d**, containing 10 mole% vanillic acid. The rise of the ^{13}C signals at 57.1 ppm (**V$_{\alpha}$**), 116.1 ppm (**V$_{\beta}$**) and 152.4 ppm (**V$_{\gamma}$**) indicate the presence of vanillic acid. Some peaks of the vanillic acid partially overlap with the peaks of HQ and HBA, e.g., the ^{13}C resonance at 127.0 ppm. It can further be seen that the intensity of the $^{13}C\{^{1}H\}$ CP/MAS NMR spectra decreases upon heating above the glass transition temperature (Figure S4a). This can be attributed to cold-crystallization of the sample, as also observed in DSC analysis. Flexibility of the phenyl rings and aliphatic spacers in this polymer occur already at 90 °C, which is close to the onset of melting. Interestingly, only the methoxy group of VA (**Vα**) becomes mobile at 90 °C, while the phenyl ring of VA (**V$_{\beta}$** and **V$_{\gamma}$**) becomes mobile at 110 °C and higher as is visible in both the $^{13}C\{^{1}H\}$ CP/MAS and $^{13}C\{^{1}H\}$ INEPT MAS NMR experiments in

Figure S4a and S4b. In fact, it is expected that the presence of the methoxy group of VA hinders the rotational motion of the VA phenyl ring and restricts its motion. Interestingly, since the mobile methoxy group does not affect the mobility of its neighboring groups, it can be concluded that the T_m decreasing effect of vanillic is can only be attributed to the sterical hindrance of the methoxy group that inhibits crystallization.
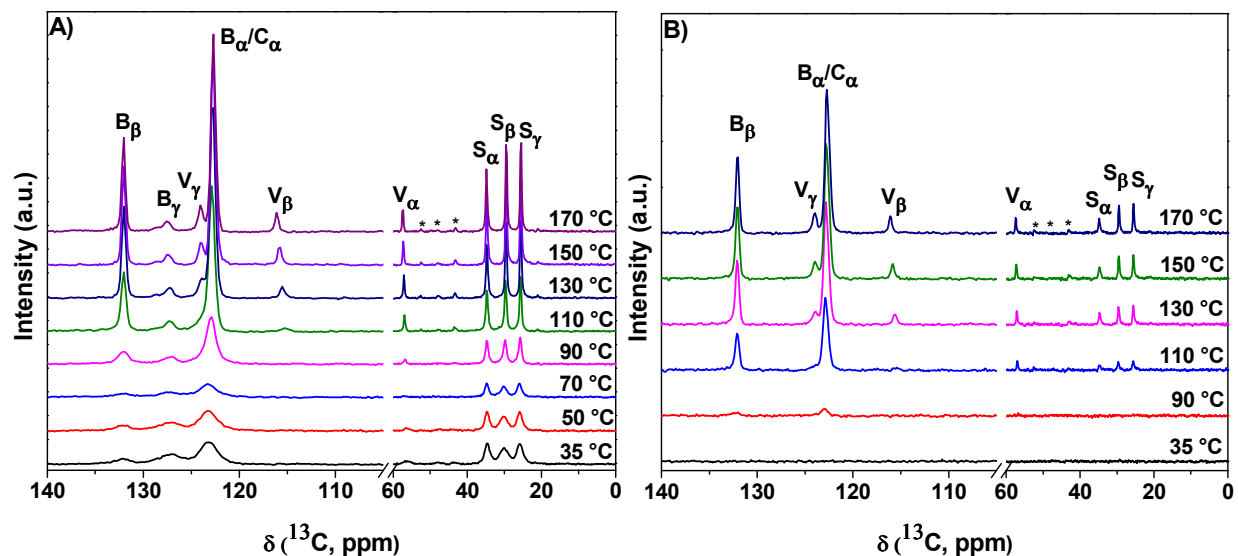

Figure S4: Temperature-dependent solid-state $^{13}C\{^1H\}$ CP/MAS NMR (**A**) and $^{13}C\{^1H\}$ INEPT MAS NMR (**B**) results obtained for sample **4d**. Signals denoted with an asterisk are spinning sidebands, whereas the assignment follows that of Scheme S1. All experiments were recorded at 11.75 T (500.13 MHz for ^1H) using a MAS frequency of 10.0 kHz and ^1H decoupling during acquisition.

[i] C.H.R.M. Wilsens, B.A.J. Noordover, S. Rastogi, unpublished work