Supplemental Information

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1. ^1H-^1H COSY

COSY NMR spectra for PEPs revealed a range of resonances attributed to CH_3, $–CH_2$- and –CH-X (X: C or O) groups (Fig. S1a) and cross peaks of sp^3-hybridized carbon on aromatic rings (phenyl-CH-). Cross peaks of sp^3- hybridized aliphatic carbon attached to an oxygenated group such as $HC_{sp}{}^3(O)$-$C_{sp}{}^3$-H, H-$C_{sp}{}^3(O)$-$C_{sp}{}^3(O)H$) and/or ester-derivatives (R(=O)O-$C_{sp}{}^3H_2$-$C_{sp}{}^3H(C_{sp}{}^3H_3)$-R(or OR)) (Fig. S1b, and cross peaks of aliphatic saturated alcohols (R-CH_2-OH) (Fig. S1c) were also observed. In the aromatic region, cross peaks at δ_H (F1: δ_H 6.80 ppm and F2: δ_H 7.11 ppm; Fig. S1b) may be associated with non-exchangeable hydrogen in *o*- and *m*- position of a styrene ring. The lack of coupling with these cross peaks at δ_H 6.80 and δ_H 7.11 ppm was indicative of the absence of 4-vinylpyridine-styrene-like derivatives. Cross peaks resonances of sp^2-hybridized aromatic carbon in extended aromatic systems with up to several aromatic rings were also observed (Fig. S1e). The COSY NMR spectra of toner powder demonstrated convoluted cross-peaks in the aliphatic region reflecting multiple intra-aliphatic correlations (*e.g.*, CH-CH_x-C_nH-CH_x-C, n=1,2 and x varies depending on n) probably due to the polymer-based chemicals in the powder. Cross peaks attributed to non-exchangeable organic hydrogen bonded to sp^2-hybridized carbon in α,β- oxygenated olefins (R-CH_2-$C_{sp}{}^2H$=$C_{sp}{}^2H$-O-X (X: C or H)). The aromatic range of toner powder COSY NMR spectra (Fig. S1) also depicted the convoluted methylene cross peaks associated with the polymeric material centered in resonances previously attributed to non-exchangeable organic hydrogen atoms in styrene (Fig. S1). No cross peaks indicative of hydrogen atoms in extended aromatic rings were observed.

2. ^1H-^1H TCOSY and NOESY

The TCOSY NMR spectra for PEPs showed fewer resonances attributed to methyl groups (H_3C-CH-X, where X=C or O; Fig. S2a) and cross peaks of oxygenated aliphatics (O-CH-CH-O) in the δ_H 3.4-4.5 ppm region (Fig. S2b). Poorly resolved cross peaks in the aliphatic and aromatic regions were indicative of intra-aliphatic correlations within the same spin system (C-CH-C_nH-CH-C, n = 0 - 4) (Fig. S2b) and/or substituted extended aromatic systems. A small fraction of non-exchangeable organic hydrogen bound to aromatic sp^2-hydridised carbon showed cross peaks in the δ_H 7.0 – 8.0 ppm may be attributed to carboxylic (COO-) and carbonyl (CHO) derivatives (Fig. S2c) as it is further indicated by the HMBC NMR spectra. The TCOSY NMR spectra of toner powder further confirmed the presence of long chain unsaturated alcohols in the toner powder and a strong styrene-based signature. NOESY NMR spectra of PEPs and toner powder (Fig. S3) depicted cross peaks of methyl, methylene and allylic non-exchangeable organic hydrogen in the carbohydrate and aromatic regions (Fig. S3a, b). A fewer number of cross peaks was observed in the aromatic region (Fig. S3c). The reduced number of resonances may be indicative of chemical species with relatively linear or planar structures that reduces the correlation of hydrogen atoms in space.

3. ^{1}H-^{13}C HSQC

The HSQC NMR spectra of PEPs and toner powder demonstrated strong similarities in the aromatic region (*i.e.*, $\delta_{H/C}$ 7.0 – 8.0/105 – 135 ppm; Fig. S4) and significant differences in the carbohydrate (*i.e.*, $\delta_{H/C}$ 3.5 – 6.0 /55 – 80 ppm; Fig. S4) and aliphatic (*i.e.*, $\delta_{H/C}$ 0.0 – 3.5/0 – 55 ppm; Fig. S4). The majority of cross peaks in PEPs HSQC NMR spectra was associated with sp^3-hybridized carbon as compared to toner powder HSQC. Terminal methyl (C-CH_3) NMR (Fig. S4a) accounted for most of the C-CH_3 integrals (Fig. S4a,b). spectra that demonstrated a stronger signature of aliphatic sp^2-hybridized carbon. Intensive, predominantly for toner powder and to a lesser extend for PEPs, cross-peak resonances in the $\delta_{H/C}$ 5.0 – 5.5 /65 – 75 ppm assigned to aliphatic chain methylene (-C-CH_2-C) in close proximity (a-position) or further away of COX groups (Fig. S4c,d). In the carbohydrate region, cross-peaks in PEPs HSQC NMR spectra were minimal and reflected resonances of both sp3- and aromatic sp2-hybridised carbon attached to a hydroxyl group. For toner powder, stronger COX signatures were also observed in addition to resonances in the $\delta_{H/C}$ 3.5 – 6.0 /55 – 80 ppm; Fig. S4 attributed to sp^2-hybridized carbon (R_2C=CH). (cross peaks show direct coupling between Carbon and Hydrogen. The Carbon in the 100-150 ppm are attributed to aromatic or R_2C=CR_2 functional groups. For styrene, C2 and C6 resonate at 113.85 ppm and C3 and C5 at 127.53. The peak at 1.60 ppm was attributed to $CH_2\beta$ of styrene and is coupled with the Cβ signal at 31.05 ppm in the HSQC. The HSQC spectrum shows no cross peaks with any of the proton signal suggesting that Cα is quaternary. The Carbon signal at 156.41 ppm was attributed to the C4 carbon of the styrene aromatic ring. Substitution with an alkyl ether is responsible for the shift of the signal to higher field compared to C4 unsubstituted resonance around 120-130 ppm. The HMBC spectrum shows cross peaks with C4 and the styrene aromatic protons in the ortho and meta position (6.80 and 7.11 ppm) as well as cross peaks with signals at 4.28, 4.14, 4.08, 3.91 and 3.77 ppm that come from protons in α position of an oxygen (ether, ester or carbonyl group). C_1 at 143.58 ppm was also coupled with H_3 and H_5 protons at 6.80 ppm and methylene $C_\beta H_2$ proton at 1.60 ppm. The C_β is coupled with peaks at 1.28 ppm and 0.88 ppm that are attributed to branched methyl in alpha carbon of the polymer backbone.

4. ^1H-^{13}C HMBC

In the HMBC spectrum, the protons of methylene in β position is also coupled with Cα (41.72 ppm) and C_1 (143.58 ppm) of styrene (C_1 links the aromatic ring and aliphatic backbone).

The COSY spectrum show couplings with peaks at 4.13 and 1.47 ppm. The HMBC spectrum show coupling between the carbon at 165.28 and the proton signal at 5.48 suggesting that the propylene group is linked to an ester group. The H proton at 1.25 ppm is coupled to the Carbon at 29.71 ppm and is attributed to methylene protons (CH_2) in aliphatic backbone and branched chains of polyester polymers. The COSY show a cross peak between 1.25 and 0.88 (CH_3) ppm and is attributed to chain of poly aliphatic compound. In the HSQC this signal is coupled to the Carbon at 129.64 ppm and in the HMBC it is coupled with signals at 134.13 ppm and at 165.28 ppm that corresponds to an ester (-C=O(O)-) or amide (R-CONHR) protons. This fits well with ^{13}C NMR spectra of terephthalic acid found in the literature. Also, the peak at 165.28 ppm is coupled with the proton signal at 5.48 ppm, it is linked to the propylene unit. The COSY doesn't show any coupling with the peaks at 6.80 and 7.11 ppm ruling out the possibility of 4-vinylpyridine-stryene copolymer that presents the same type of signature in the aromatic region of the NMR spectrum. In the HSQC this signal is coupled to the Carbon at 129.64 ppm and in the HMBC it is coupled with signals at 134.13 ppm and at 165.28 ppm that corresponds to an ester (-C=O(O)-) or amide (R-CONHR) protons. This fits well with ^{13}C NMR spectra of terephthalic acid found in the literature. Also, the peak at 165.28 ppm is coupled with the proton signal at 5.48 ppm, it is linked to the propylene unit.

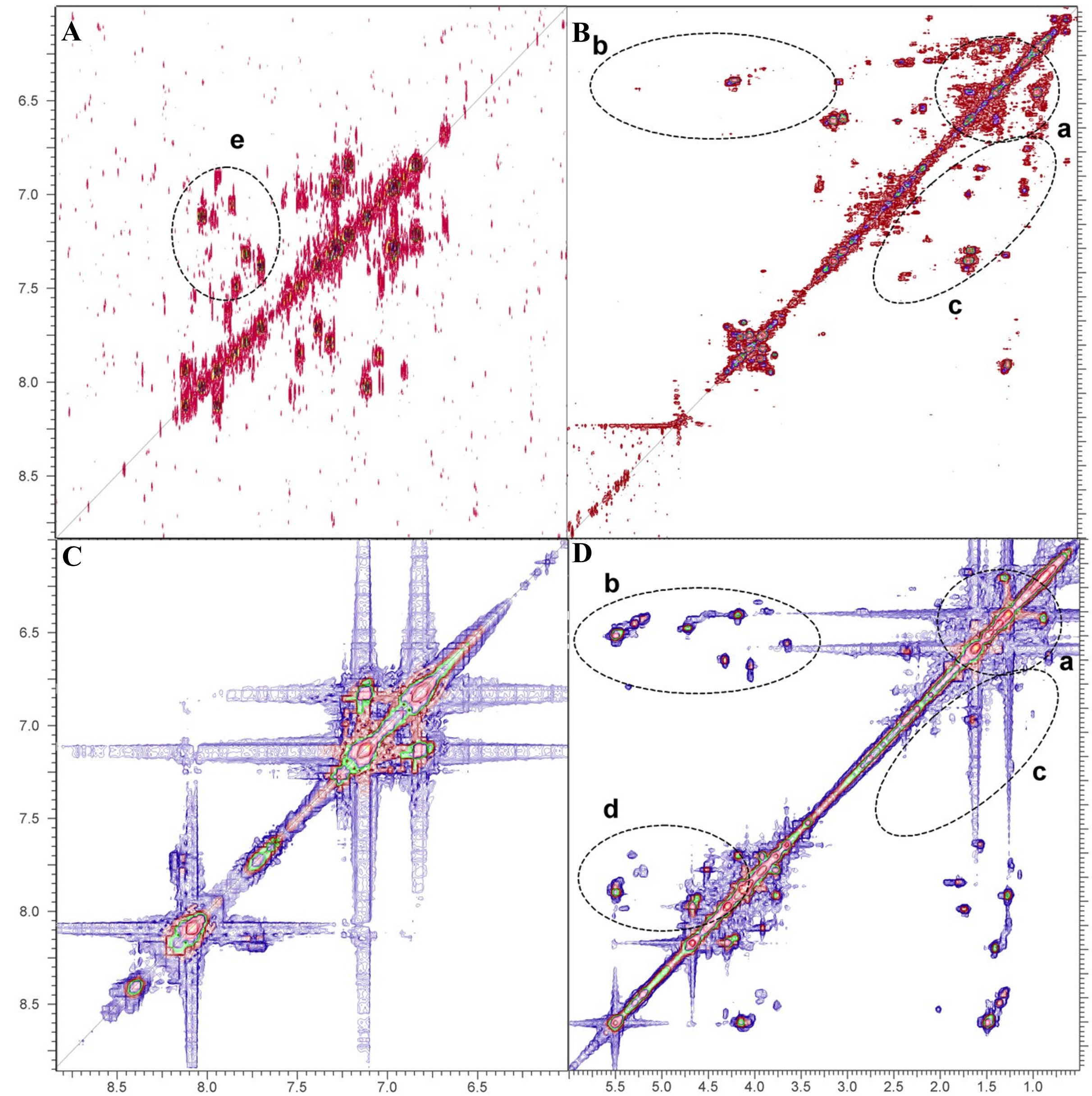

Figure S1. ^{1}H-^{1}H COSY NMR spectra of PEPs ($PM_{2.5}$) (A,B) and toner powder (C,D): aromatic region (δ_H = 5.5–9.0 ppm; aromatic and olefinic cross peaks); aliphatic and carbohydrate region (δ_H = 0.5–.0 ppm; aliphatic cross peaks).

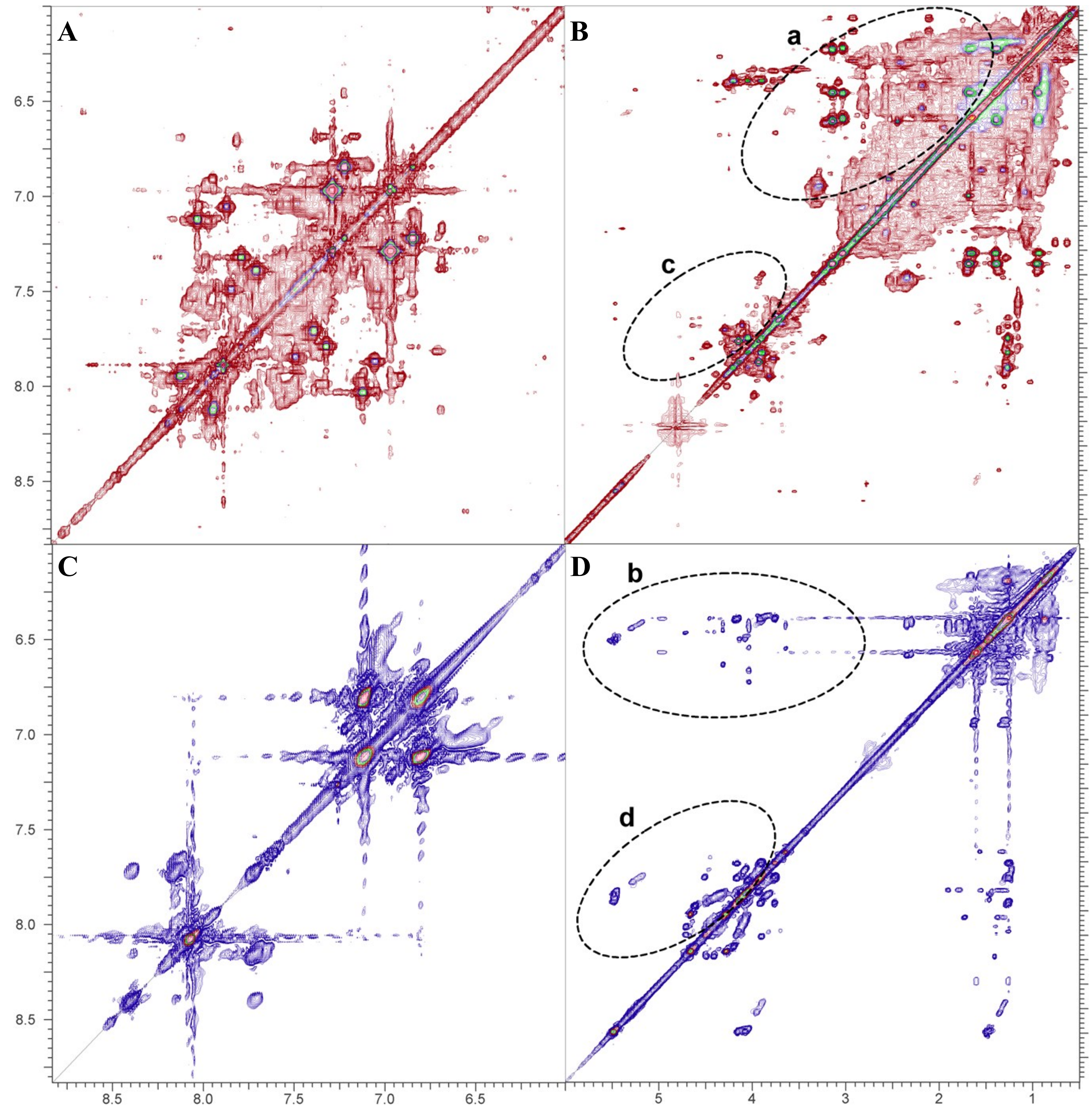

Figure S2. ^{1}H-^{1}H TCOSY NMR spectra of PEPs ($PM_{2.5}$) (A,B) and toner powder (C,D): aromatic region (δ_H = 5.5–9.0 ppm; aromatic and olefinic cross peaks); aliphatic and carbohydrate region (δ_H = 0.5–.0 ppm; aliphatic cross peaks).

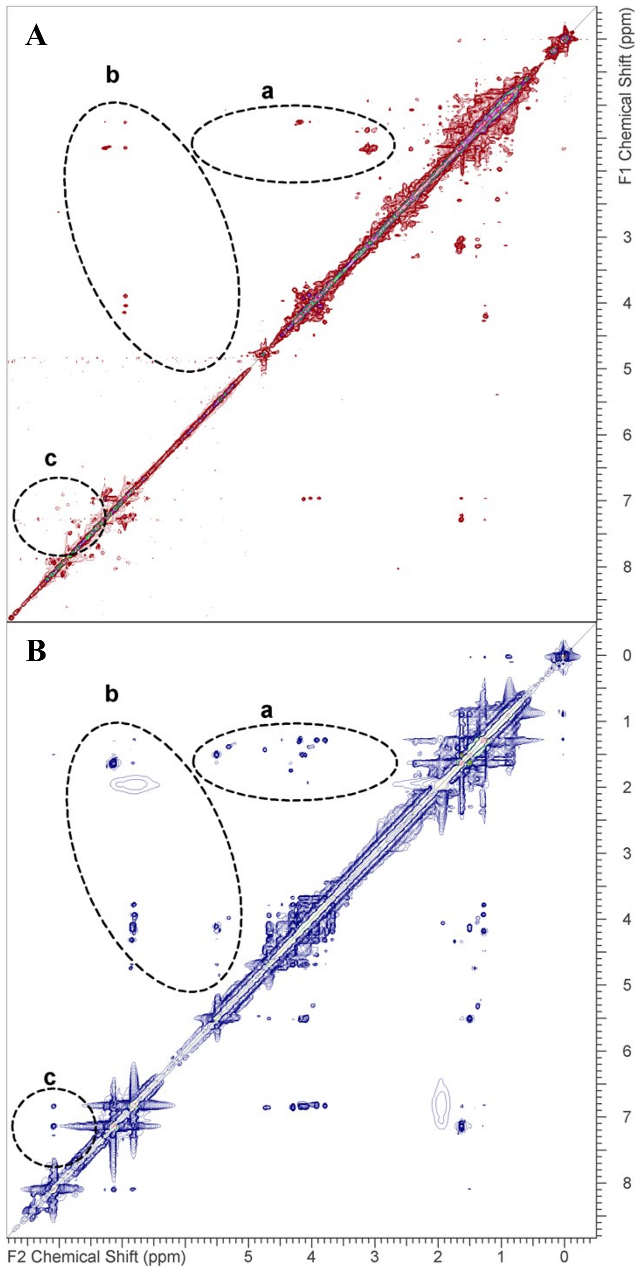

Figure S3. ^{1}H-^{1}H NOESY NMR spectra of PEPs ($PM_{2.5}$) (A) and toner powder (B).

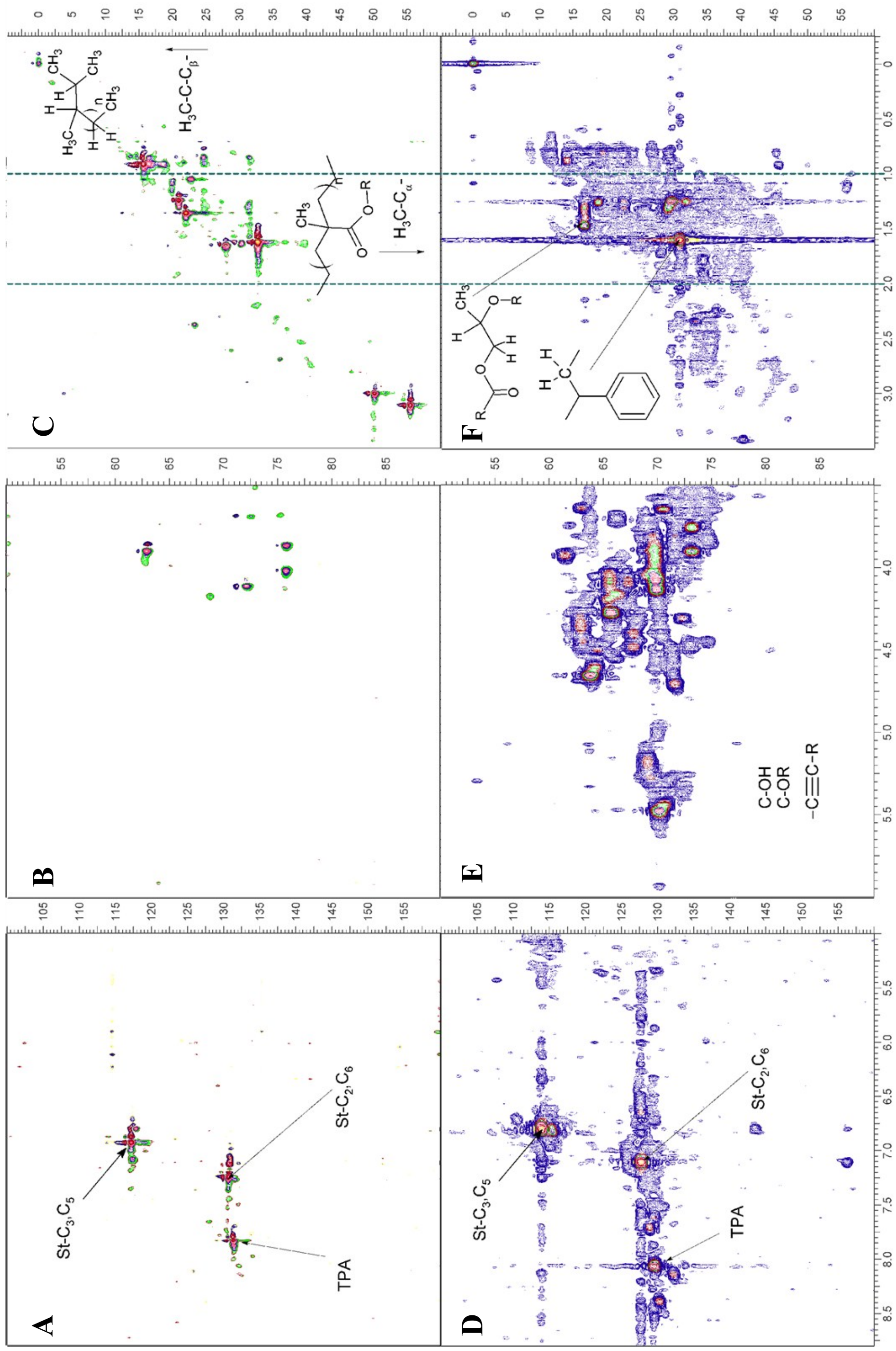

Figure S4. ^{1}H-^{13}C HSQC NMR spectra of PEPs ($PM_{2.5}$) (A,B,C) and toner powder (D,E,F): aromatic region (δ_H = 5.5–9.0 ppm/ δ_c = 50–90 ppm; aromatic and olefinic cross peaks); carbohydrate region (δ_H = 5.5–9.0 ppm/ δ_c = 100–160 ppm; alcohols, ethers and esters cross peaks); aliphatic region(δ_H = 0.5–4.0 ppm/ δ_c = 0–55 ppm; aliphatic cross peaks)

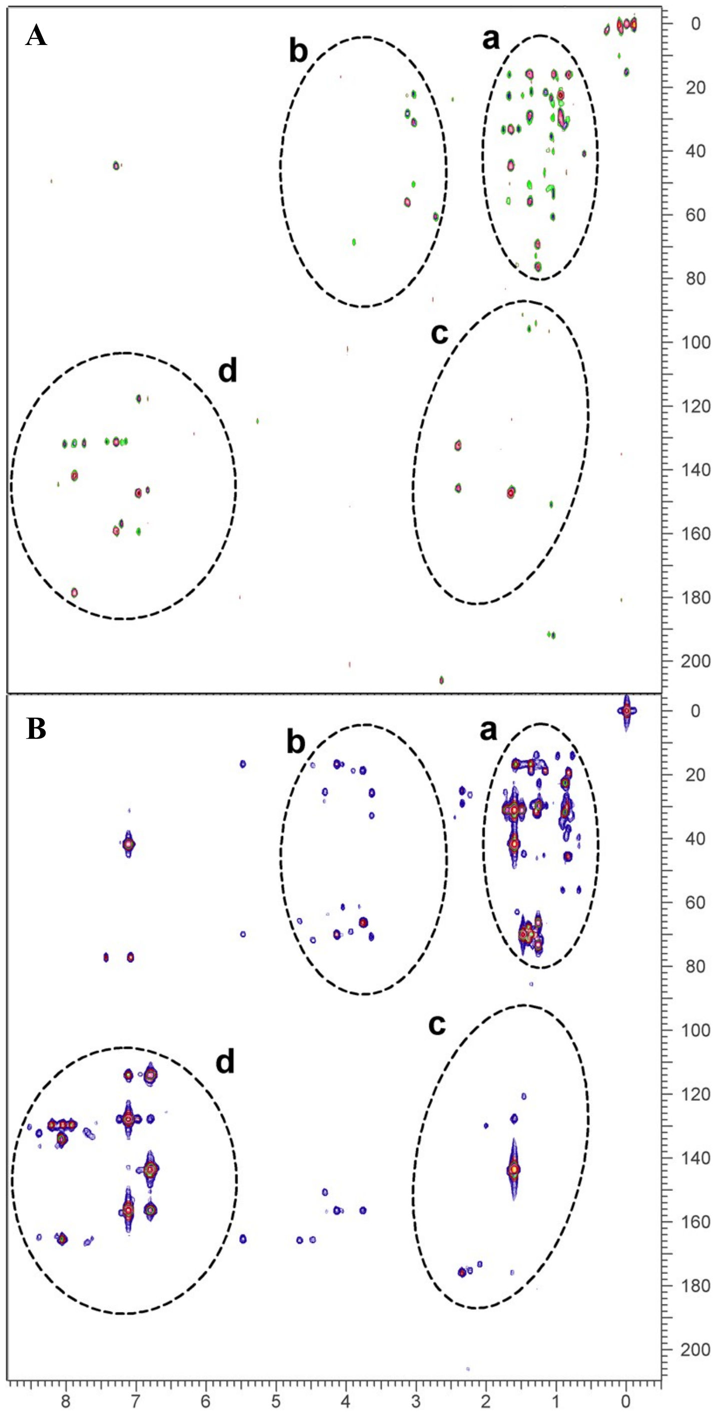

Figure S5. ^1H-^{13}C HMBC NMR spectra of PEPs ($PM_{2.5}$) (A) and toner powder (B).

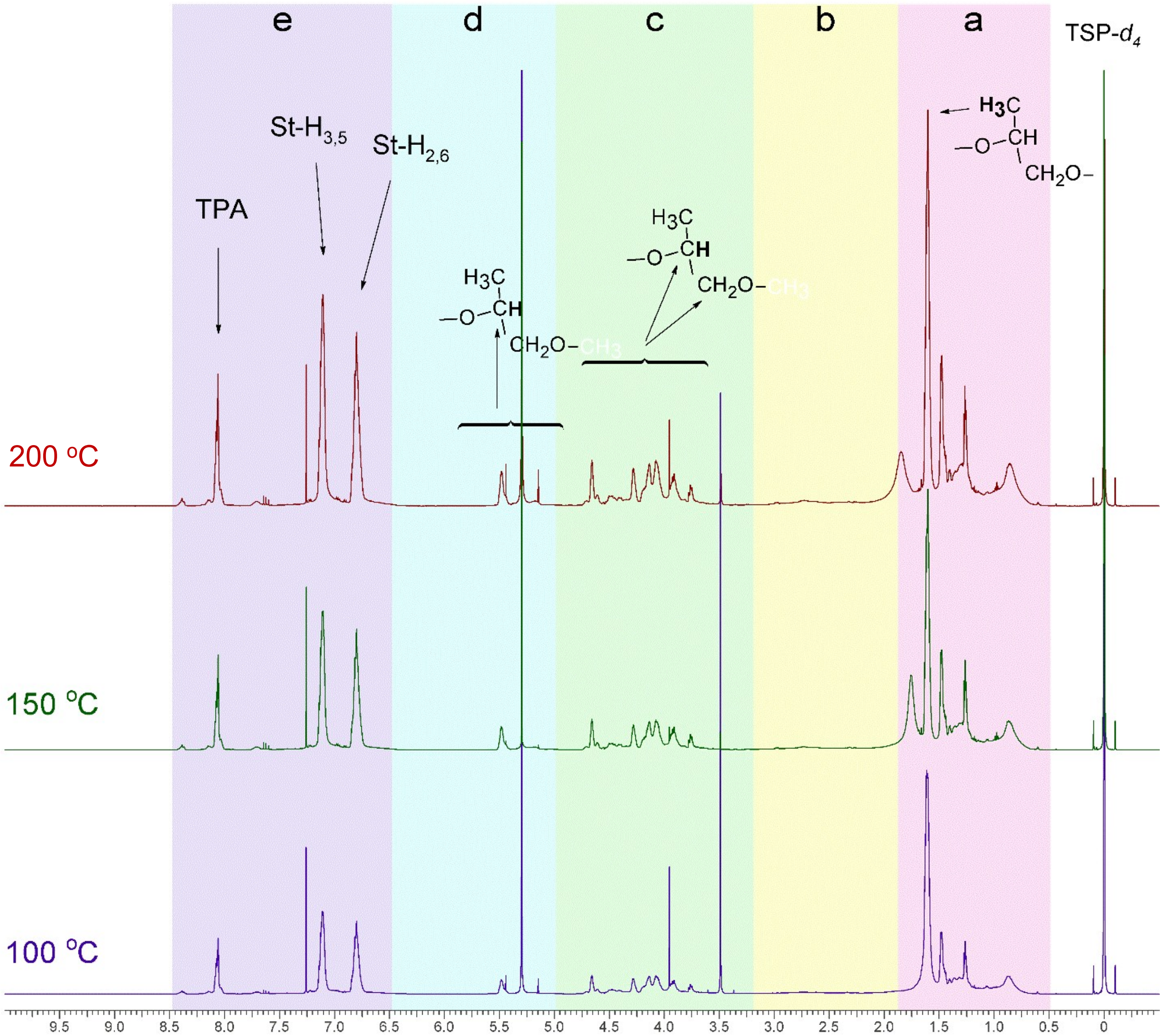

Figure S6. ^{1}H NMR spectra (δ_H 0 – 10.5 ppm) of toner powder thermally heated at 100°C, 150°C and 200°C acquired with solvent suppression and exclusion regions for residual HDO. Functional structure are indicated from right to the left: (a) aliphatic carbon (**H**CCC); (b) “allylic-analogue” (**H**C-C=X); (c) carbohydrate-like and methoxy (**H**C-O); (d) olefinic (R-C**H**=C**H**-R and O-C**H**-O); and (e) aromatic ($\mathbf{H}C_{ar}$), The respective spectral intensities were scaled to 100% total integral within the entire region of chemical shift (δ_H 0.7–10.5 ppm; with residual water excluded).