Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Enzymatic synthesis of electrospinnable poly(butylene succinate-co-dilinoleic succinate) thermoplastic elastomer

Águeda Sonseca[1], Miroslawa El Fray[1]*

[1]Division of Biomaterials and Microbiological Technologies, Polymer Institute, West Pomeranian University of Technology, 45 Piastów Ave. 70-311, Szczecin, Poland

Dimer diols or dimeric fatty alcohols are formed by reduction of the terminal groups of the corresponding dimer fatty acid. PRIPOL 2033 is a high purity dimer linoleic diol, fully hydrogenated and distilled aliphatic dimer alcohol with purity of 96.5 %. It has to be taken into account that as in the commercial dimeric fatty acids from CRODA, in the case of the dimeric fatty alcohols, their main structure is a mixture of linear (acyclic) and cyclic dimer alcohols and their isomers, that contains in a small amount some impurities as trimers, oligomers, unsaturations or unreacted monomers.[1,2] Some possible structures are shown in **Figure S1**. Chemical structure of PRIPOL 2033 was verified by ^{1}H NMR and ^{13}C NMR and peaks were assigned to one of the most common structures. The results are presented in **Figures S2** and **S3** respectively.

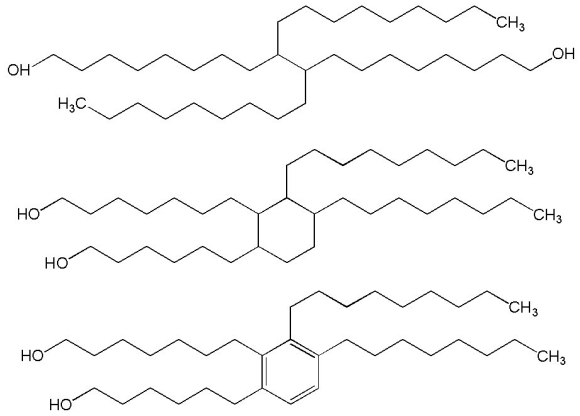

Figure S1. Some possible structures of PRIPOL 2033 dimeric fatty alcohol.

Regarding the ^{1}H NMR (**Figure S2**), the singlet at $\delta^{1}H$ = 1.70 ppm (exchangeable with D_2O) is due to the hydroxyl end groups. Resonances at $\delta^{1}H$ = 1.49-1.61 ppm (f, g) correspond to the tertiary carbon protons and the methylene units attached to the $–CH_2OH$ group. The triplet at $\delta^{1}H$ = 3.63 ppm (h) is due to the methylene units attached to the –OH terminal group. Resonances at $\delta^{1}H$ = 1.26 ppm (b, c, d, e, j) correspond to methylene protons attached to the methyl group and the rest of methylene protons, and resonances at $\delta^{1}H$ = 0.83-0.87 ppm (a) correspond to methyl protons. The resonances in the interval of $\delta^{1}H$ = 6.7-7 ppm can be related with the presence of aromatic protons which is in agreement with the appearance of the signal at $\delta^{1}H$ = 2.54 ppm

referred to a methylene protons adjacent to an aromatic moiety, and with the fact that no peaks were detected in the region of δ^1H = 5-6 ppm where unsaturation in aliphatic chains are having place.

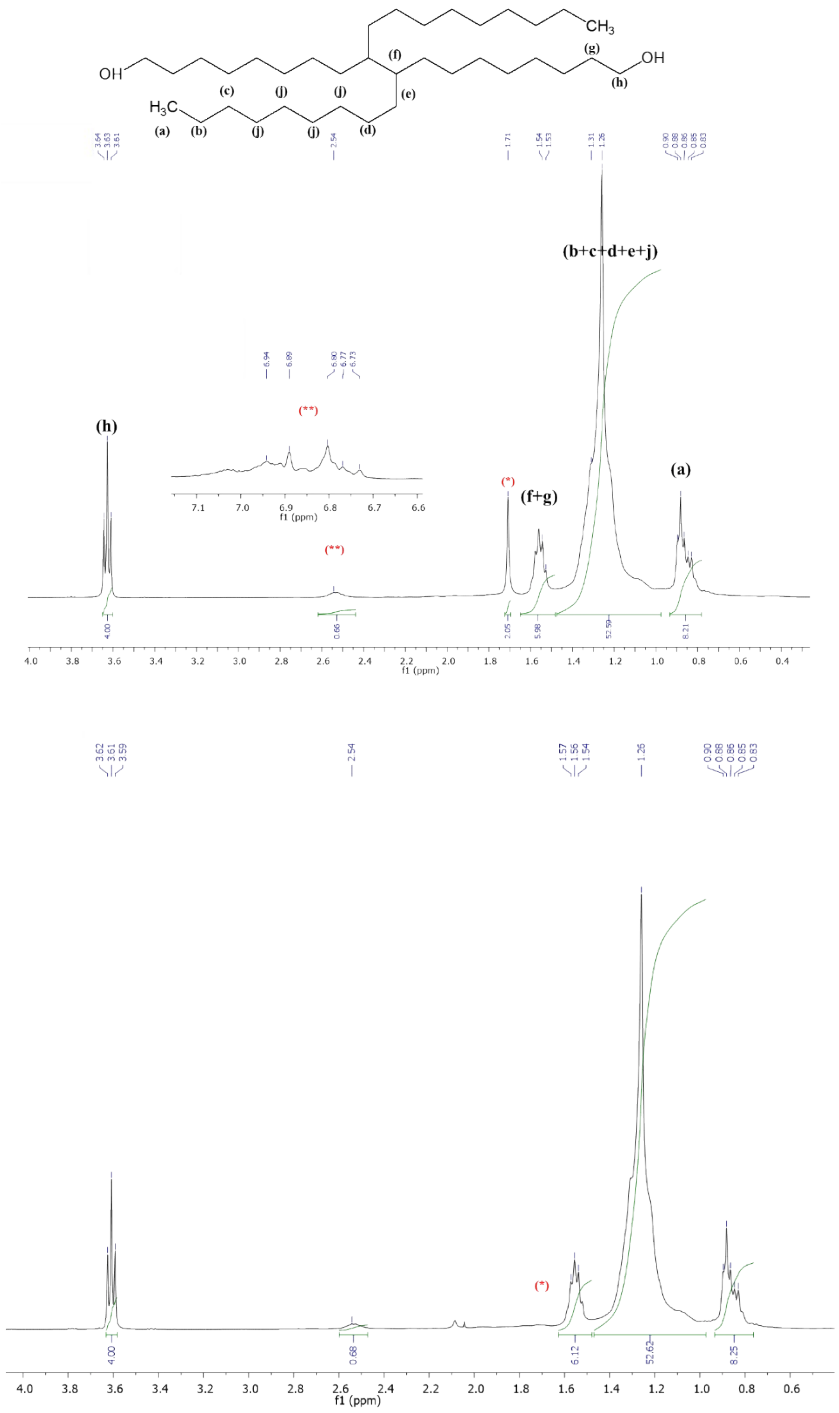

Figure S2. Top; ^1H NMR of PRIPOL 2033 in $CDCl_3$. Bottom; ^1H NMR of PRIPOL 2033 in $CDCl_3$ with one drop of D_2O.

Regarding the ^{13}C NMR (**Figure S3**), the peak at $\delta^{13}C$ = 14.15 ppm is due to the $-CH_3$, $\delta^{13}C$ = 22.71 ppm is due to the CH_2-CH_3, $\delta^{13}C$ = 25.77 ppm is due to the $-CH_2-CH_2-CH_2$-OH, $\delta^{13}C$ = 29.39-29.72 ppm is due to the $-CH_2-$, $\delta^{13}C$ =30.18 ppm is due to the $-CH_2-$ attached to the tertiary carbons, $\delta^{13}C$ =31.95 ppm is due to the $-CH_2-CH_2-CH_3$, $\delta^{13}C$ = 32.81 ppm is due to the $-CH_2-CH_2$-OH, $\delta^{13}C$ = 37.4 ppm is due to the tertiary carbons, and $\delta^{13}C$ = 63.02 ppm is due to the $-CH_2$-OH. In agreement with the ^1H NMR, the signals at $\delta^{13}C$ = 26.71, $\delta^{13}C$ = 33.69 ppm and $\delta^{13}C$ = 37.12 ppm can be related with the presence of aliphatic chains linked to a cyclic aliphatic structures or aromatic rings and the resonances at $\delta^{13}C$ = 19.74 ppm can be related to methyl carbons different from the ones from the end groups. In addition, the signal at $\delta^{13}C$ = 37.12 ppm can be related with the presence of $-CH_2-$ adjacent to an aromatic carbon in agreement with the observations from ^1H NMR.

It should be pointed out that high spectrum amplitude for ^1H NMR and ^{13}C NMR was employed to observe the protons and the carbons not present in the main structure proposed since they represent only a small portion of the total dimer structures present in the PRIPOL 2033.

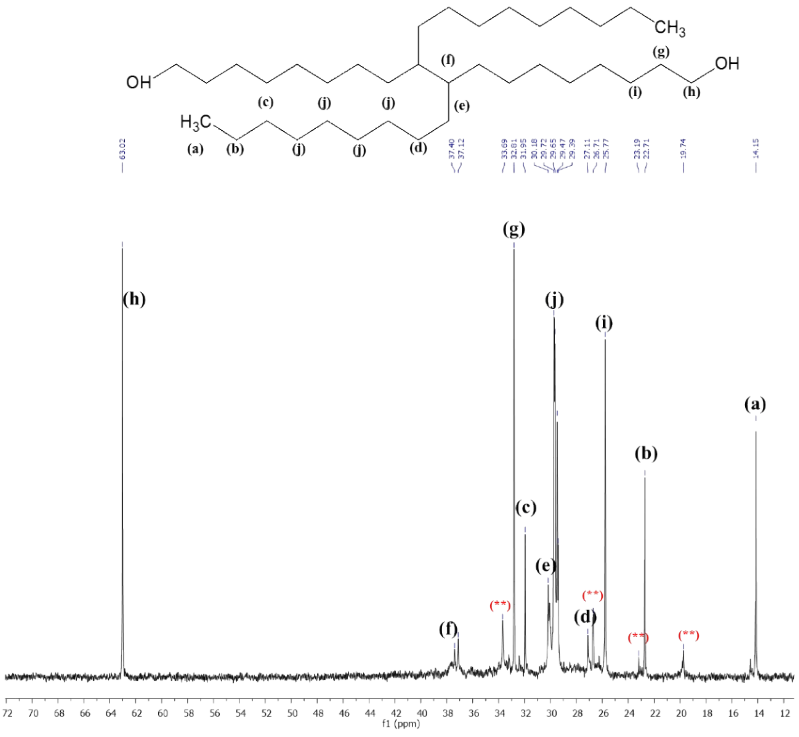

Figure S3. ^{13}C NMR of PRIPOL 2033 in $CDCl_3$.

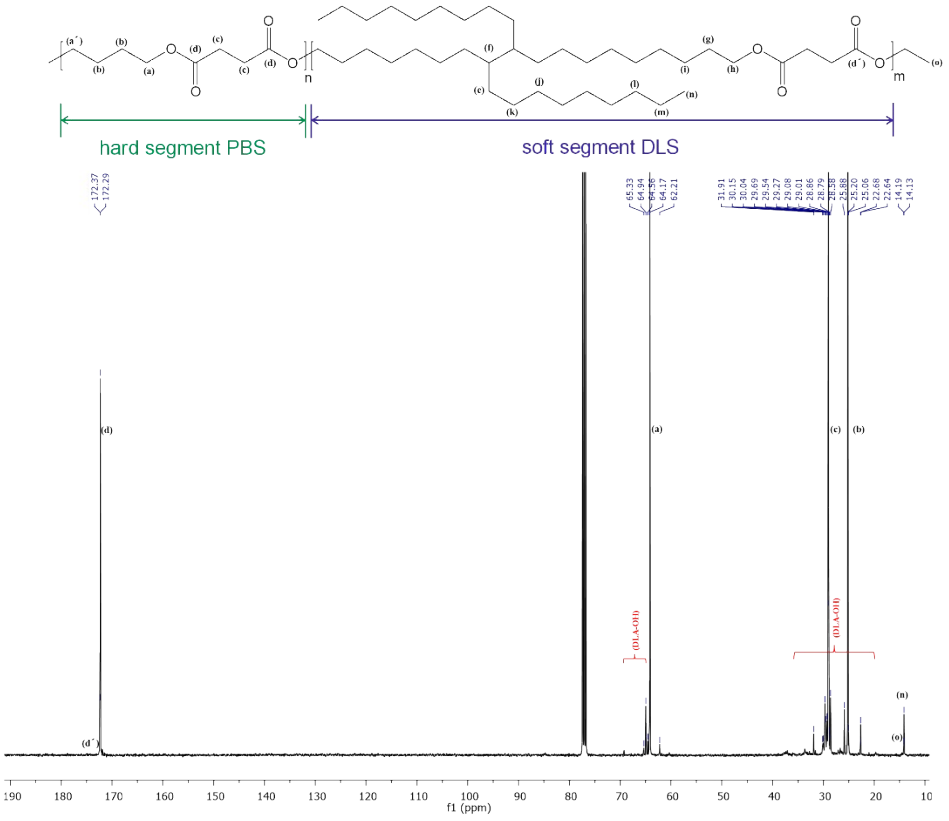

Figure S4. ^{13}C NMR of the poly(butylene succinate-co-dilinoleic succinate) 70:30 copolymer.

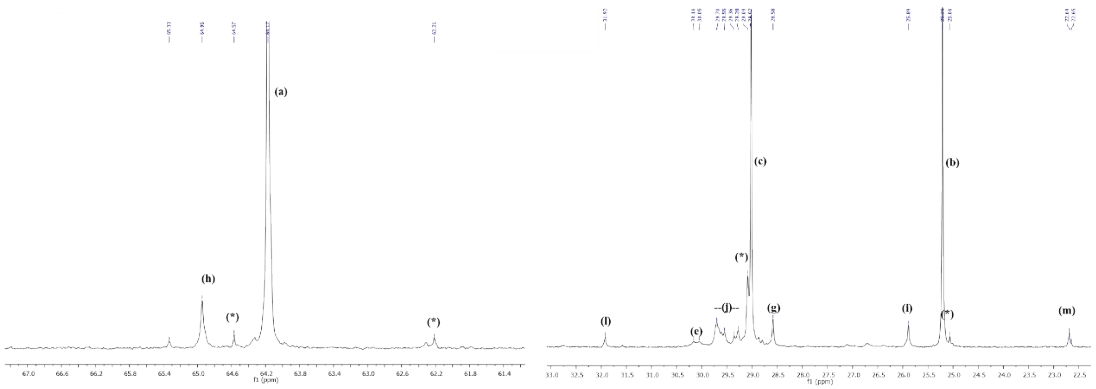

Figure S5. ^{13}C NMR of the poly(butylene succinate-co-dilinoleic succinate) 70:30 copolymer. Regions from 22.5-33.0 ppm and 61.4-67.0 ppm.

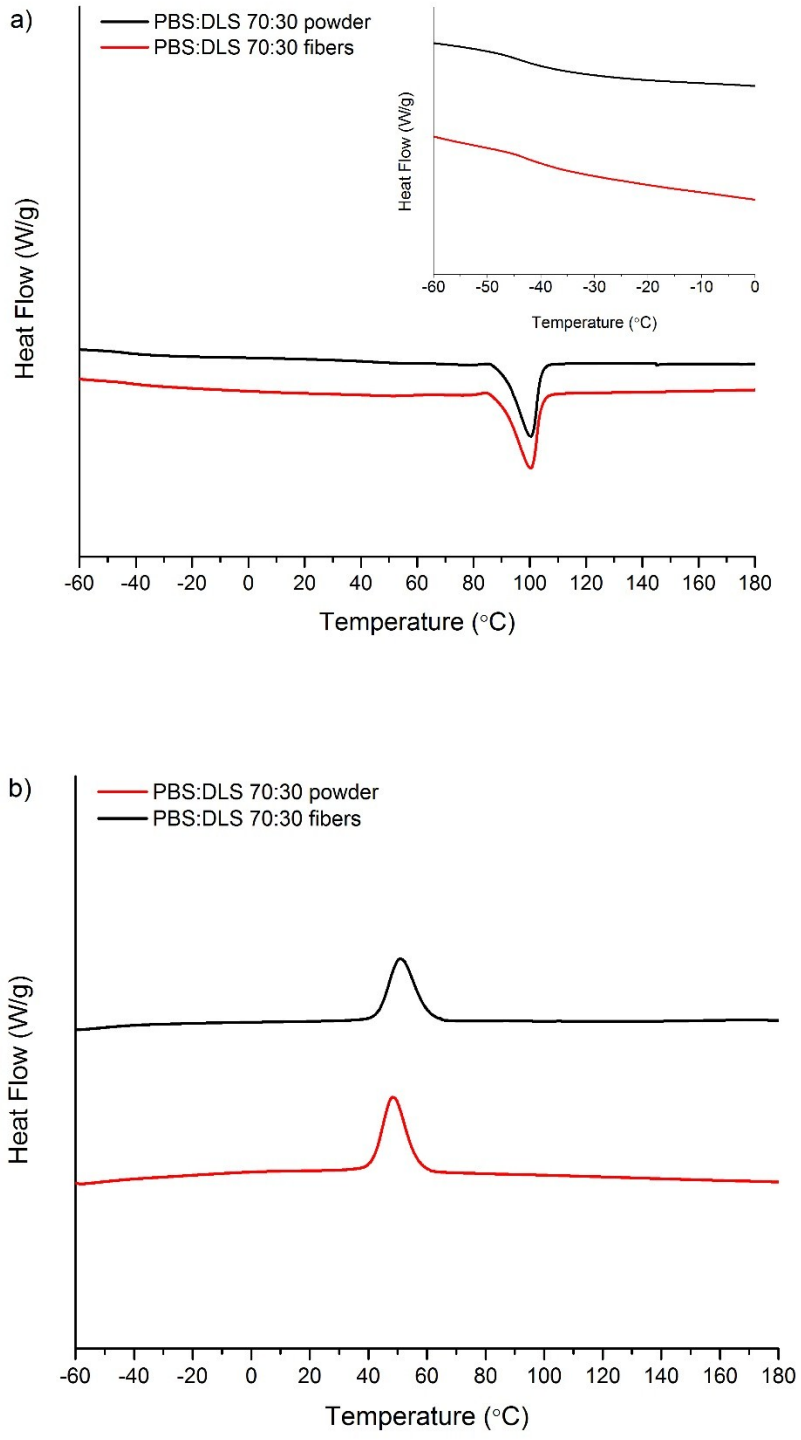

Figure S6. DSC thermograms of bulk and electrospun PBS:DLS 70:30 copolymer. Second heating (a) and cooling (b).

References

1. A. Piegat, PhD thesis, West Pomeranian University of Technology Szczecin, 2010.

2 J. Skrobot, PhD thesis, West Pomeranian University of Technology Szczecin, 2014.