

One-pot synthesis of PET-based plasticizer and tetramethyl thiuram monosulfide (TMTS) as vulcanization accelerator for rubber production

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S2. Materials and Methods

S2.4 Synthesis of raw materials and LA/EG/PET/PG/LA plasticizer

S2.4.1 Synthesis of 1,2-propanediol (propylene glycol; PG)

γ -Al₂O₃ (Across) was impregnated with Cu(NO₃)₂·3H₂O water solution [10 ml_{solution}/g(Al₂O₃)] to obtain catalysts with 20 wt.% of copper loading. The solvent was removed by air bubbling; the samples were afterward heated in at 110 °C for 12 h and calcined at 700 °C for 5 h [1].

Glycerol hydrogenolysis reaction to 1,2-PD was conducted in a stainless steel autoclave equipped with a stirrer, inlet and sampling tube as well as release valve (Parr reactor, 500 ml). Prior to the reaction start, the prepared Cu/Al₂O₃ catalyst was reduced in 10% H₂/N₂ at 250 °C for 3h. 100 g of glycerol (Sigma Aldrich, 99.5%) and 10 g of a pre-reduced catalyst were loaded into the autoclave. The autoclave was pressurized with H₂, (Praxair 99.999%) to 5 MPa. The reactor was heated to 220 °C, and the speed of the stirrer was set constant at 100 rpm throughout the reaction. The initial reaction pressure was observed to increase with the elevated temperature and reached its maximum when the temperature reached the desired value. After that, the pressure decreased slowly with the reaction time, indicating hydrogen consumption during the reaction. After 6 h, reaction was finished, and the autoclave was cooled down to an ambient temperature with an ice-water bath for 20 min, followed by depressurization. Liquid-phase product was centrifuged to remove the solid catalyst powder and purified by fractional vacuum distillation.

The boiling point was 183-186 °C. FTIR, cm⁻¹: 3311 ν (O-H stretch), 2973-2868 cm⁻¹ ν (C-H stretching of –CH₃ and –CH₂ groups), 1460, 1412, 1375 cm⁻¹ δ (C-H bending of –CH₃ and –CH₂ groups and O-H bending), 1137, 1033 cm⁻¹ ν (C-O stretches), 989-832 cm⁻¹ δ (C-H bending of of –CH₃ and –CH₂ groups out-of -plane). FTIR spectrum of PG is presented in Figure S1.

[1] Pussana Hirunsit, Chuleeporn Luadthong, Kajornsak Faungnawakij, Effect of alumina hydroxylation on glycerol hydrogenolysis to 1,2-propanediol over Cu/Al₂O₃: combined experiment and DFT investigation, RSC Advances 5 (2015) 11188, DOI: 10.1039/c4ra14698k

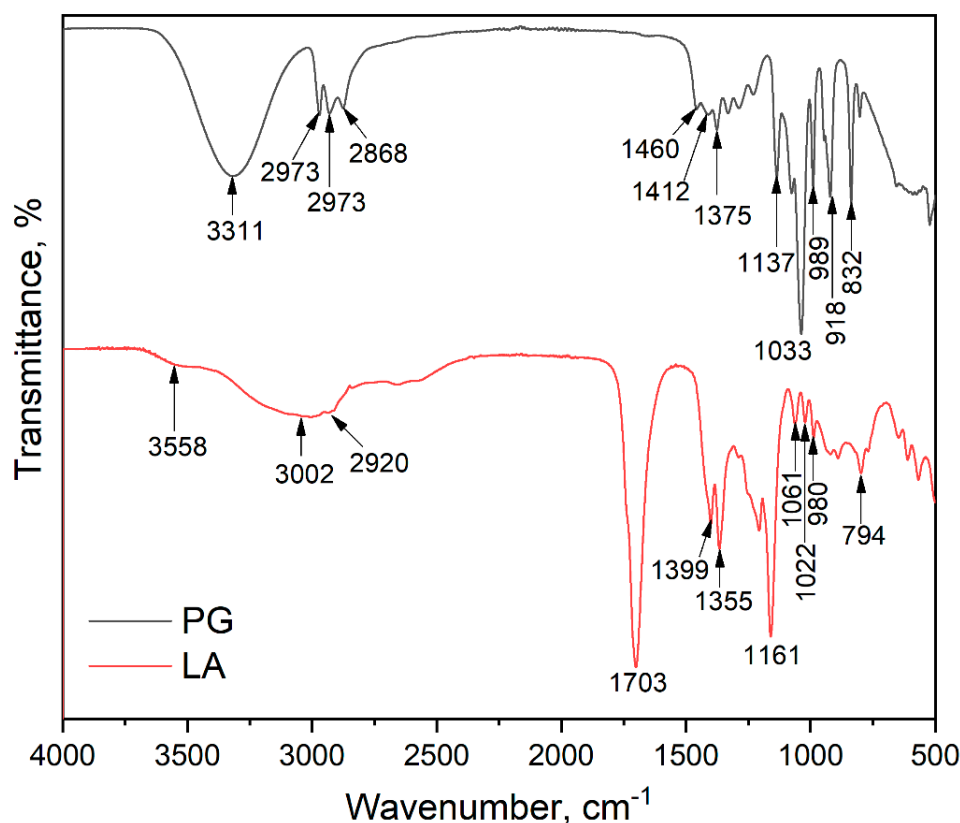


Figure S1. FTIR spectrum of PG and LA

S2.4.2 Synthesis of Levulinic acid (4-oxopentanoic acid)

LA production starting from Fructose was performed at the following condition: 30% of fructose solution was acidified with 0.1 M HCl to pH 0.5 and transferred to vial G30 (Eppendorf AG, Hamburg, Germany). Operational condition: temperature 160 °C, power 800W, time 5 minutes and pressure 15 bar. After purification yield of LA was 62% [2]. The larger quantity of the material necessary for industrial production was provided by suppliers.

Melting point 31-33 °C. Elemental analysis agrees within 0.3% with the calculated value. FTIR, cm^{-1} : 3558-3002 $\nu(\text{O-H stretch})$, 2920 cm^{-1} $\nu(\text{C-H stretching of } -\text{CH}_3 \text{ and } -\text{CH}_2 \text{ groups})$, 1703 cm^{-1} $\nu(\text{C-H stretching of C=O group})$, 1399, 1355 cm^{-1} $\delta(\text{C-H bending of } -\text{CH}_3 \text{ and } -\text{CH}_2 \text{ groups and O-H bending})$, 1161, 1061-980 cm^{-1} $\nu(\text{C-O stretch})$, 989-832 cm^{-1} $\delta(\text{C-H bending of } -\text{CH}_3 \text{ and } -\text{CH}_2 \text{ groups out-of-plane})$. FTIR spectrum of the obtained LA product is presented in Figure S1. $^1\text{H NMR}$ (500 MHz, D_2O) δ = 2.15 (s, 3H, C(5) H_3), 2.52 (t, 2H, C(2) H_2), 2.80 (t, 2H, C(3) H_2); $^{13}\text{C NMR}$ (125 MHz, D_2O) δ = 213.7 C(4), 177.4 COOH, 37.8 C(3), 29.2 C(2) and 27.9 C(5).

[2] Rabab Salih, Zlate Veličković, Milena Milošević, Vera P. Pavlović, Ilija Cvijetić, Ivana V. Sofrenić, Jelena D. Gržetić, Aleksandar Marinković, Lignin based microspheres for effective dyes removal: Design, synthesis and adsorption mechanism supported with theoretical study, Journal of Environmental Management, 326 (2023) 116838, <https://doi.org/10.1016/j.jenvman.2022.116838>

S2.4.3 Synthesis of plasticizer based on 2-((4-oxopentanoyl)oxy)ethyl 4-(4-methyl-6,9-dioxodecanoyl)benzoate structure ($n=1$) (named LA/PG/PET/EG/LA)

In a three-necked flask, (500 ml) equipped with a reflux condenser, mechanical stirrer, and thermometer were added 36 g of PG and 0.8 g of FASCAT 4100 catalyst with gentle mixing (50 o/min). Then 97 g of PET was gradually added to the flask to provide PET melting by raising the temperature to 230/240 °C continuing with more intensive mixing of the reaction mixture (150 rpm). Reaction was performed for 9 h. In the second, 59 g of LA was added, and after 4 hours, 0.21 ml of TBT was added dropwise. Water was extracted from the system using a Din-Stark extension. The reaction was performed at 160 °C. The most convenient structure of the obtained product is given on Figure S2.

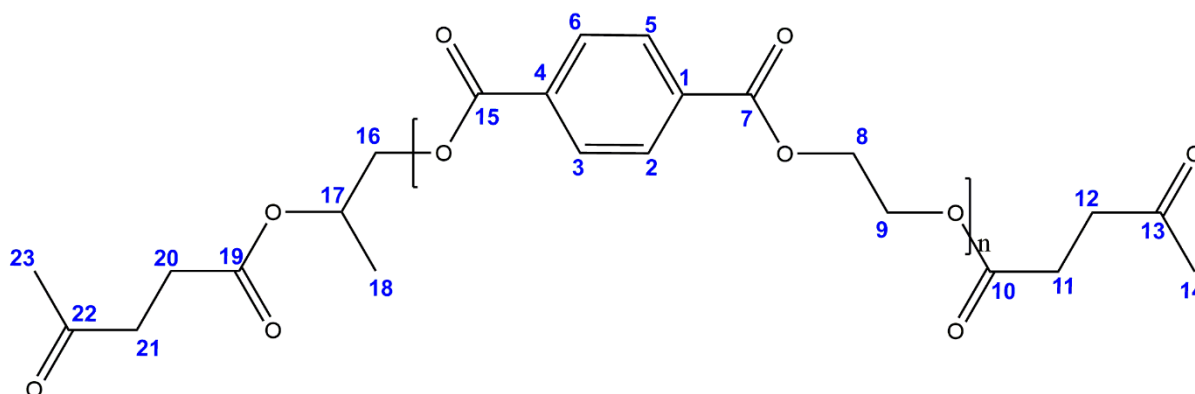


Figure S2. The most convenient structure of synthesized plasticizer LA/PG/PET/EG/LA

Elemental Analysis (calculated), %: C, 59.48; H, 6.08; O, 34.45

Elemental Analysis (determined), %: C, 59.66; H, 5.98; O, 34.36

S2.5 Rubber blend production

Formulations of rubber blends based on NBR and SBR rubber with 20 phr of commercial (DINP) and synthesized bio/PET-based plasticizers are shown in Tables S1 and S2.

Table S1 Rubber products composition with 20 phr of plasticizers based on NBR 28% acrylonitrile content

Formulation/component	NBR₀	NBR₁	NBR₂	NBR₃
Plasticizer	DINP	LA/PG/PET/EG/LA	DINP	LA/PG/PET/EG/LA
NBR 28%	100	100	100	100
Stearic acid	1.4	1.4	1.4	1.4
Faktis	5.2	5.2	5.2	5.2
VULKANOX MB-2/MG	2.5	2.5	2.5	2.5
Carbon black N-550	53	53	53	53
VULKANOL FH	5.2	5.2	5.2	5.2
Plasticizer	20	20	20	20
ZnO	5.2	5.2	5.2	5.2
6PPD	2	2	2	2
Sulfur	2.8	2.8	2.8	2.8
VULKACIT CBS	1.6	1.6	1.6	1.6
TMTD	0.4	0.4	-	-
TMTS	-	-	0.4	0.4

Table S2 Rubber products composition with 21 phr of plasticizers based on SBR rubber

Formulation/component	SBR₀	SBR₁	SBR₂	SBR₃
Plasticizer	DINP	LA/PG/PET/EG/LA	DINP	LA/PG/PET/EG/LA
Ravaflex™ SBR /1500	100	100	100	100
Stearic acid	2	2	2	2
Precipitated Silica	30	30	30	30
PDA ^a	5.2	5.2	5.2	5.2
Plasticizer	21	21	21	21
ZnO	5	5	5	5
Sulfur	2	2	2	2
VULKACIT CBS	1.2	1.2	1.2	1.2
TMTD	0.5	0.5	-	-
TMTS	-	-	0.5	0.5

^a PDA - p-substituted phenilene diamine

Rubber compounds (2 kg) were mixed in a Haake Rheocord System 90, manufactured by Haake, Germany, according to the following procedure:

In the first step, SBR caoutchouc was added and followed, following by the addition of

1. after 10 s, half the quantity of filler, ZnO, and stearic acid,
2. 100 s Silica and plasticizer,
3. 360 s PDA, Vulkacit CBS, TMTD/TMTS, and sulfur,
4. 420 s finishing of the compounding in the mixer,
5. 600 s, Homogenization on three roll mill, 3 to 5 minutes
6. 900 s, production of the sheet 5 mm thick 5 mm, and conditioning at 20-22 °C for 24 h

Parameter recorded in the course of compounding: temperatures of the mixture and of the environment (mixer housing and rotor) as a function of time, as well as torque, cumulative energy used for mixing, and the number of revolutions of the rotor per minute. The initial temperature was 40 °C, the speed was 50 rpm, and the fill factor (the ratio of the volume of the mixture to the volume of the space of the mixer chamber) was 0.6. When forming on two rollers, the gap between the rollers was from 0.2 mm to 2 mm, the friction between the rollers was about 1.3, and the mixing time was from 3 to 5 minutes. After 24 h of conditioning, the mixtures were cross-linked at 170 °C and at the optimal cross-linking time, tc90.

The cross-linking process of the mixture based on SBR and the combination of active fillers, monitored using a rheometer with an oscillating disc, Haake Mars II, manufactured by Thermo Fisher Scientific, Germany), was expressed through the following parameters: scorch time, ts2, optimal cross-linking time, tc90, cross-linking speed index (English cure rate index - CRI), minimum torque, M_L, and maximum torque, M_H (table 4). The parameters were determined during cross-linking of the mixture at temperatures of 150 °C and 170 °C.

S2.6 Characterization methods

Melting points were determined on a SMP30 Melting point apparatus. Elemental analyses (C, H, N) were performed by the standard micromethods using the ELEMENTAR Vario EL III CHNS/O analyzer. Fourier Transform Infrared spectra (FTIR) of compounds were recorded on ATR-FTIR Nicolet iS10 (Thermo Scientific) spectrometer in the range 4000-500 cm⁻¹ with a resolution of 4 cm⁻¹ at room temperature. NMR spectra were recorded in CDCl₃ on a Bruker Avance III 500 spectrometer equipped with a broad-band direct probe at 500 MHz. The spectra were recorded at room temperature. Chemical shifts are given on a scale relative to tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were recorded on a mass spectrometer system. The UV absorption spectra were measured in range of 200-800 nm using Shimadzu 1700 UV/vis spectrophotometer. The UV spectra of 1×10⁻⁵ mol dm⁻³ solutions of TMTD and TMTS in methanol at 25°C.

Moisture was determined by material heating at 110 °C until the constant weight of the material.

Ash content was determined according to ASTM D5667 using a furnace with a max 1300 °C.

Determination of heavy metals was performed using Atomic Absorption spectrophotometer Spectra AA 55 (Varian).

The standard methods applied for the determination of the mechanical properties of obtained rubber product are given in Table S3.

Table S3 The standard methods used for the determination of physico-mechanical characteristics of rubber product

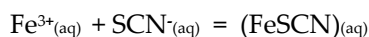
Physico-mechanical characteristics of rubber	Standard	
Shore hardness (°ShA)	SRPS G.S2.125	DIN 53505
Tensile strength (MPa)	SRPS G.S2.127	ISO 37
Stress at 100% elongation (MPa)	SRPS G.S2.127	ISO 37
Stress at 300% elongation (MPa)	SRPS G.S2.127	ISO 37
Elongation at break (%)	SRPS G.S2.127	DIN 53479
Density	ASTM D297	ISO 2781

The determination of indentation hardness of a durometer (hardness Shore A) of the obtained samples was scaled in degrees (1-100).

Tensile strength, elongation at break, and Stress at 100% and 300% elongation of rubber samples were performed using an AG – X plus Universal testing machine, Shimadzu. All tests were performed at room temperature and adjusted at a crosshead speed of 0.5 mm/min.

Determination of thiocyanate ion (colorimetric method)

Determination of thiocyanate ion was based on the following reaction



By comparing the intensity of the color (red) of this solution with the colors of a series of standard solutions with known Fe^{3+} concentrations, the concentration of thiocyanate ion in the filtrate was determined.

Reagents:

- Ferric ammonium sulfate $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ standard solutions ($2, 4, 6, 8$, and $10 \times 10^{-5} \text{ mol L}^{-1}$ for calibration curve construction)
- 1 mol L^{-1} sulfuric acid
- 1 mol L^{-1} hydrochloric acid
- 0.15 mol L^{-1} potassium permanganate solution

At a predefined time of reaction, the sample was taken and filtered. The volume of the thiocyanate solution was measured (adjusted to obtained reading in the calibration curve range).

After 15 minutes of addition of Iron solution, absorbance at a wavelength of 490 nm was measured using a colorimeter, and concentration was determined graphically and by calculation.

The method developed for the determination of the percentage of pure TMTS content in the synthesized product

Based on the examination of the validity of Beer's law for a solution of TMTS in methanol for a specific working wavelength (276.4 nm), a graph was constructed (Figure S3). From the graph shown in Figure S3, it can be seen that Beer's law is valid for the concentration range from 1×10^{-5} to $1 \times 10^{-4} \text{ mol/dm}^3$. Therefore, the absorbance is a linear function of the concentration of the TMTS solution in methanol in the concentration range from 1×10^{-5} to $1 \times 10^{-4} \text{ mol/dm}^3$. After this conclusion, a new, working graph was constructed (Figure S3; red line). The graph represents the linear dependence of the absorbance on the concentration of TMTS for the defined range of concentrations. Based on the working graph, it is possible to determine the unknown concentration (c_X) of the prepared sample for a certain absorbance value read on the UV-spectrophotometer. Based on the reproducible results obtained in the laboratory conditions of the optimization of the TMTS synthesis reaction in one pot, an industrial trial production was carried out. The technological scheme of carrying out the industrial production of TMTS is shown in Figure 1.

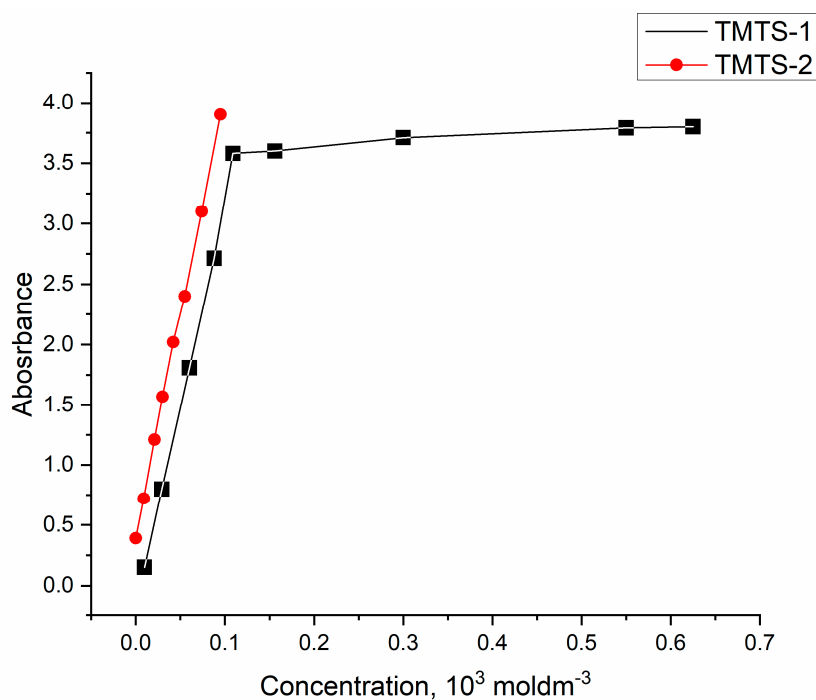


Figure S3. Dependence of absorbance on TMTS concentration

Characterization of zinc-bis(dimethyldithiocarbamate) (Ziram): evidence for the reaction mechanism

The structure of Ziram is given in Figure S4:

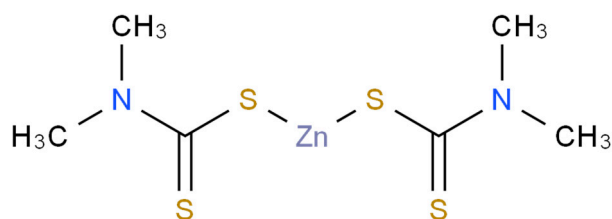


Figure S4. Zinc-bis(dimethyl dithiocarbamate) structure

Analysis (purity, moisture content, pH) of Ziram

1) Analysis of purity

Apparatus and materials:

- flask, 500ml
- condenser with funnel
- adsorber for additional hydrogen sulfide (the first adsorber)

- adsorber for carbon disulfide (the second adsorber)
- erlenmeyer flask, 500ml
- buret, 50ml

Reagents:

- 10% lead acetate, aqueous solution.
- 2M potassium hydroxide, methanol solution.
- 30% acetic acid, aqueous solution.
- 1M sulfuric acid, aqueous solution.
- 0,05M standard solution of iodine.
- 1% starch, aqueous solution.
- 1% phenolphthalein, ethanol solution.

Procedure:

Weigh 0.5 - 0.6 g of the sample (Ziram) in dry flask (250 ml). Add an aqueous solution of lead acetate (20-25 ml) into the first adsorber and an aqueous solution of potassium hydroxide (20-25 ml) into the second adsorber. The apparatus and reaction flask is connected over the condenser. In the reaction flask, add sulfuric acid through the funnel of the condenser, and connect vacuum so that the three bubbles per second pass through the adsorber. After an hour and half of boiling, drop down the content of the second adsorber into an Erlenmeyer flask (500 ml) and wash using distilled water. In obtained solution, add one to two drops of phenolphthalein, neutralize with acetic acid, and titrate using an iodine solution. In the end, add starch and continue titration. The end point of the titration is identified as the first permanent trace of a dark blue-black color.

Calculation:

$$\% \text{ Ziram} = \frac{V(\text{ml}) \cdot 0.05\text{M I}_2 \cdot F \cdot 0.05\text{M I}_2 \cdot E \cdot 100}{G}$$

V(ml) = volume of the standard solution of iodine

F = factor of iodine solution

E = equivalent of Ziram

G = weight of Ziram

2) *Analysis of moisture content*

The infrared dryer (type Mettler Toledo LJ16) is used to determine water or moisture content by a gravimetric method. The material is weighed and dried, which gives a constant readout of moisture content as a % moisture, % solids, or weight. The final result can be determined after a set drying time or by automatic mode (constant weight). Read weight on balance or use RS232C interface for connections to PC or LC-P45 printer (Z31,196-0) to record results.

3) *pH determination*

pH meter (type Jenco Electronics LTD Microcomputer pH-Vision 6071N) is used for pH measurement.

S3. Results

S3.3. Results of the characterization of synthesized products and isolated intermediary FTIR spectrum of Ziram is given in Figure S5:

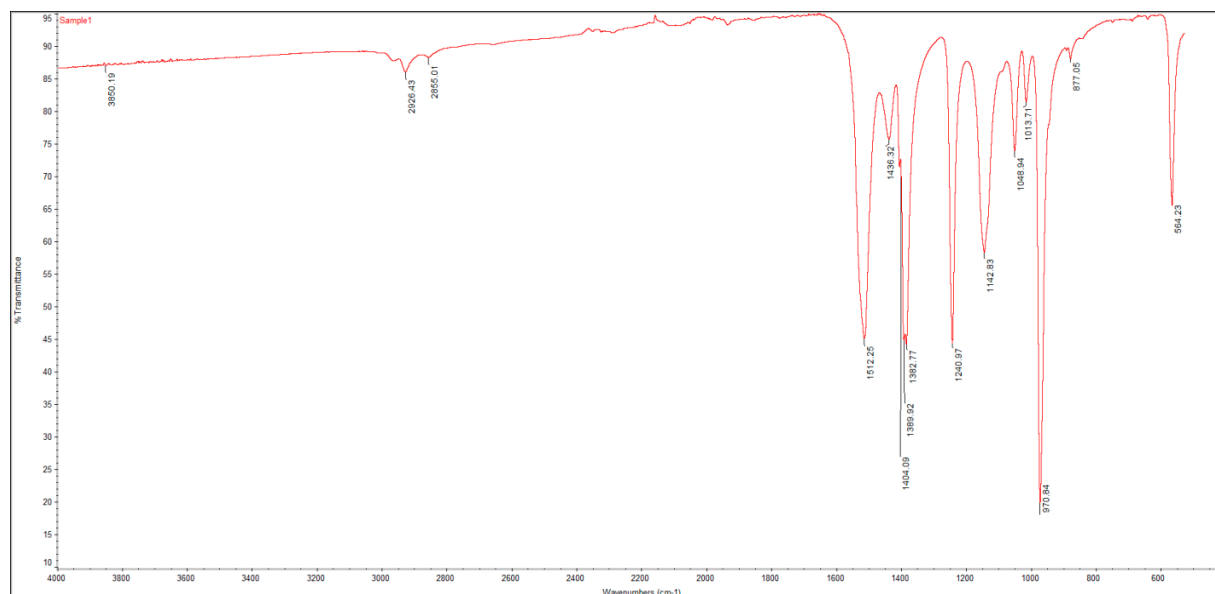


Figure S5. FTIR spectrum of Ziram (Zinc dimethyl dithiocarbamate)

S3.5 Results of the LA/EG/PET/PG/LA plasticizer synthesis

Results of the plasticizer characterization, i.e. 2-((4-oxopentanoyl)oxy)ethyl (2-((4-oxopentanoyl)oxy)propyl) terephthalate – LA/PG/PET/EG/LA, are as follow:

The results of elemental analysis, HV and AV values are given in Table S4.

Table S4. HV, AV values and results of elemental analysis of synthesized intermediary and LA/PG/PET/EG/LA plasticizers

Exp.	HV mg KOH/g	AV mg KOH/g		%C	%H	%O*
PG/PET/EG	172	1.9	Exp.	58.02	6.21	35.77
			Calc.	58.20	6.01	35.78
LA/PG/PET/EG/LA	14	4.1	Exp.	59.22	6.14	34.64
			Calc.	59.48	6.08	34.45

*Oxygen percent was calculated as subtraction

Recorded representative FTIR spectra of synthesized PET-based plasticizers are shown in Figure S6. FTIR spectroscopy was used for the identification of the structural changes after waste PET glycolysates esterification with LA. The absence of hydroxyl group stretching in the region 3000-4000 cm⁻¹ suggests that esterification with LA was successful. Asymmetric and symmetric –CH₂ and –CH₃ stretching vibrations were observed in the region 2977 - 2873 cm⁻¹, while corresponding bending vibrations appeared between 1500 and 1370 cm⁻¹. Stretching vibration of the ester carbonyl group was assigned to the band at 1713 cm⁻¹ in all three spectra. The main absorption bands between 1300 and 1015 cm⁻¹ are caused by asymmetric and symmetric C–O stretching vibrations from ester and ether groups.

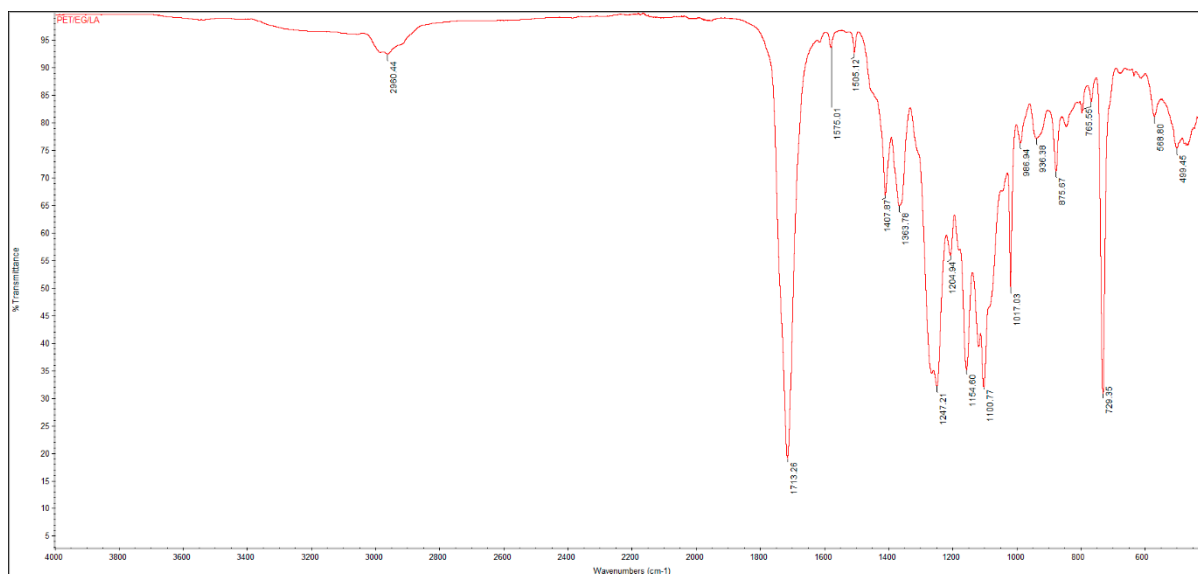


Figure S6. FTIR spectra of the synthesized waste PET-based plasticizers (LA/PG/PET/EG/LA)

Synthesis of the plasticizer, performed according to the given procedure, gave mostly inhomogeneous products, while the intention of the presented methodology was directed to the product with higher uniformity. Results of the ^1H and ^{13}C NMR analysis of the plasticizers based on PET glycolysis product with PG esterified with levulinic acid (LA) are as follows:

^1H NMR (500 MHz, CDCl_3 , δ ppm): 1.23-1.50 (*m*, 3H, C(18) H_3), 2.13-2.19 (*m*, 6H, C(14) H_3 and C(23) H_3), 2.56-2.63 (*m*, 4H, C(11) H_2 and C(20) H_2), 2.72-2.77 (*m*, 4H, C(12) H_2 and C(21) H_2), 4.05-4.71 (*m*, 6H, C(8) H_2 , C(9) H_2 and C(16) H_2), 5.11-5.58 (*m*, 1H, C(17)H), 8.07-8.11 (*m*, 4H, C(2)H, C(3)H, C(5)H and C(6)H).

^{13}C NMR (126 MHz, CDCl_3 , δ ppm): 16.41-16.69 (C(18)), 27.71-28.21 (C(11) and C(20)), 29.90 (C(14) and C(23)), 37.79-37.90 (C(12) and C(21)), 62.30-62.35 (C(8)), 63.10-63.17 (C(9)), 66.20-66.99 (C(16)), 68.50-69.58 (C(17)), 129.76-130.50 (C(2), C(3), C(5) and C(6)), 133.61-134.33 (C(1) and C(4)), 165.19-165.60 (C(7) and C(15)), 172.25-177.39 (C(10) and C(19)), 206.58-206.69 (C(13) and C(22)).

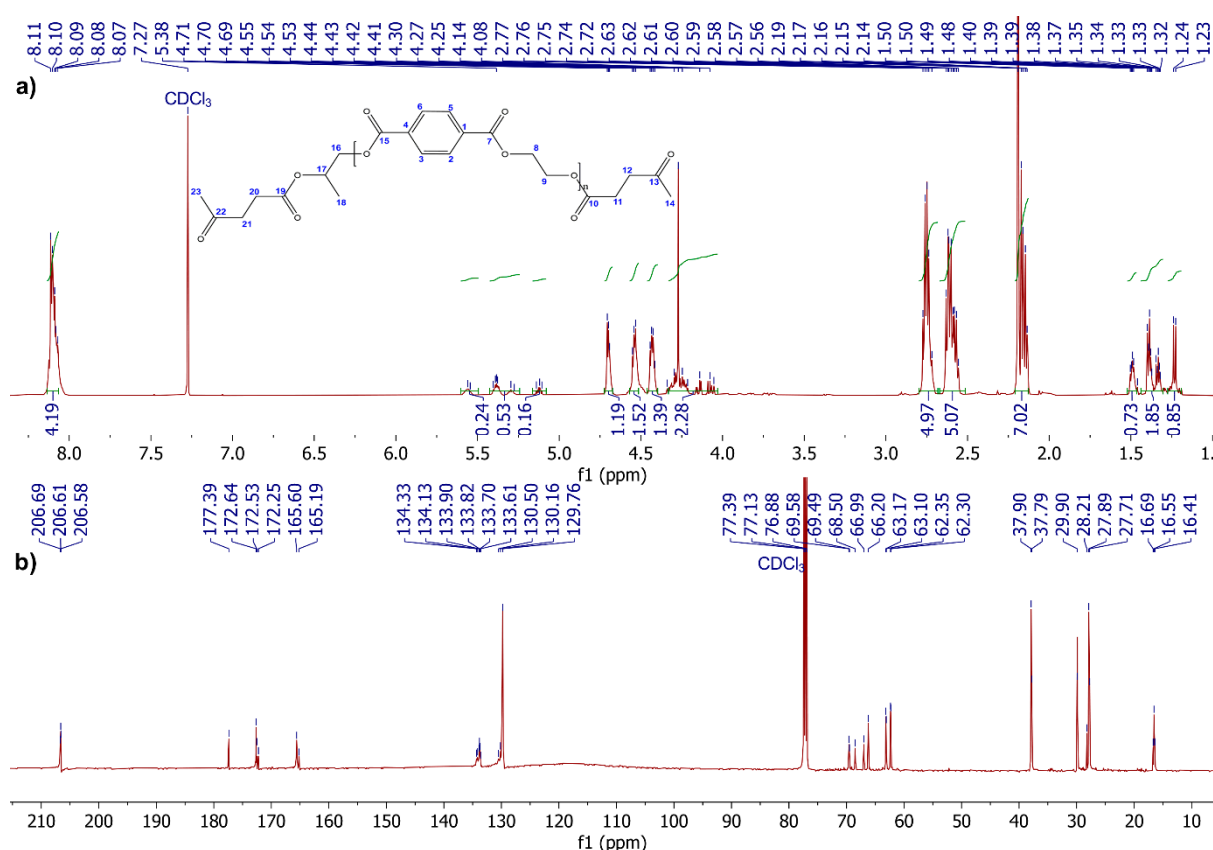


Figure S7. ^1H NMR and b) ^{13}C NMR spectra of the plasticizer LA/EG/PET/PG/LA

Except of this, disagreement of the value of integral related to C(11) H_2 and C(20) H_2 proton in the δ range 2.56-2.63, integral 5.07 (Figure S6), and C(22) H_2 and C(21) H_2 in the δ range 2.72-2.77, integral 4.97 (Figure S7), with respect to C(2)H, C(3)H, C(5)H and C(6)H protons in the δ range 8.07-8.11, integral 4.19, indicate the presence of propane-1,2-diyl bis(4-oxopentanoate) plasticizers (1,2-propanediol dilevulinate). Generation of these low molecular plasticizers arises due to lower reaction yield of 2-((4-oxopentanoyl)oxy)ethyl (2-((4-oxopentanoyl)oxy)propyl) terephthalate (or its higher condensed analogues) as a result of steric inhibition of the propylene glycol hydroxyl group nucleophilicity. Recalculating proton numbers for the plasticizer LA/EG/PET/PG/LA indicated the presence of more than 80% of 2-((4-oxopentanoyl)oxy)ethyl (2-((4-oxopentanoyl)oxy)propyl) terephthalate or analogous structure which contain 2-4 terephthalate moieties (Figure S2).