SUPPORTING INFORMATION

Chain-shattering polymers as degradable microdispersive solid-phase extraction sorbents

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Table S1.- Chemical structure and properties of the studied PAEs and DEHA.

| Analyte | Structure | Molecular formula | MM (g/mol) | Solubility in water (g/L, 25 ºC) | Vapor pressure (mmHg, 25 ºC) | Log Kow | Melting point (ºC) | Boiling point (ºC) |
|---------|-----------|------------------|-----------|---------------------------------|-------------------------------|--------|-------------------|-------------------|
| DIPP    | ![DIPP Structure](image) | C_{18}H_{26}O_{4} | 306.2     | 0.20                            | 3.54·10^{-4}                  | 5.50   | 5.50              | 336               |
| DNPP    | ![DNPP Structure](image) | C_{18}H_{26}O_{4} | 306.2     | 0.0008                          | 2.8·10^{-5}                   | 5.62   | -55               | 342               |
| DHP     | ![DHP Structure](image) | C_{20}H_{30}O_{4} | 334.4     | 0.00005                         | 1.40·10^{-5}                  | 6.82   | -58               | 302               |
| BBP     | ![BBP Structure](image) | C_{19}H_{20}O_{4} | 312.1     | 2.69                            | 8.25·10^{-6}                  | 4.73   | -35               | 370               |
| DEHA    | ![DEHA Structure](image) | C_{22}H_{42}O_{4} | 370.6     | 0.0078                         | 8.5·10^{-7}                   | 6.11   | -68               | 335               |
| DCHP    | ![DCHP Structure](image) | C_{20}H_{26}O_{4} | 330.2     | 4.0                            | 8.69·10^{-7}                  | 6.20   | 66                | 225               |
| DEHP    | ![DEHP Structure](image) | C_{23}H_{38}O_{4} | 390.3     | 0.0027                          | 1.42·10^{-7}                  | 7.60   | -55               | 230               |
| Analyte | Structure | Molecular formula | MM (g/mol) | Solubility in water (g/L, 25 ºC) | Vapor pressure (mmHg, 25 ºC) | Log Kow | Melting point (ºC) | Boiling point (ºC) |
|---------|-----------|-------------------|------------|---------------------------------|-------------------------------|---------|-------------------|-------------------|
| DNOP    | ![DNOP Structure] | C_{24}H_{38}O_{4} | 390.6      | 0.000022                        | 1.0·10^{-7}                  | 8.20    | -25               | 385               |
| DINP    | ![DINP Structure] | C_{26}H_{42}O_{4} | 419.3      | 0.0002^{d}                      | 5.40·10^{-7}                 | 9.37    | -48               | 406               |
| DIDP    | ![DIDP Structure] | C_{28}H_{46}O_{4} | 446.3      | 0.00028                         | 5.28·10^{-7}                 | 10.36   | -50               | 423               |

a) 22 ºC. b) Predicted value. c) 24 ºC. d) 20 ºC. Data taken from SciFinder® and PubChem databases. MM: Molecular mass.
Table S2.- GC-MS retention times, quantifier and qualifier m/z values of DEHA and the selected PAEs and ISs.

| Analyte | Retention time (min) | RSD values (% , n=60 injections) | Quantifier (m/z) | Qualifier 1 (m/z) | Qualifier 2 (m/z) |
|---------|----------------------|----------------------------------|------------------|-------------------|------------------|
| DBP-d<sub>4</sub> | 9.16 | 0.04 | 153 | 209 | 227 |
| DIPP | 10.08 | 0.04 | 149 | 237 | 219 |
| DNPP-d<sub>4</sub> | 10.75 | 0.04 | 153 | 223 | 241 |
| DNPP | 10.75 | 0.04 | 149 | 219 | 237 |
| DHP-d<sub>4</sub> | 12.33 | 0.04 | 153 | 255 | 237 |
| DHP | 12.33 | 0.03 | 149 | 251 | 233 |
| BBP | 12.43 | 0.04 | 149 | 91 | 206 |
| DEHA | 12.72 | 0.03 | 129 | 112 | 147 |
| DCHP | 13.79 | 0.03 | 149 | 167 | 249 |
| DEHP-d<sub>4</sub> | 13.91 | 0.03 | 153 | 283 | 171 |
| DEHP | 13.91 | 0.03 | 149 | 167 | 279 |
| DNOP | 15.28 | 0.03 | 149 | 167 | 279 |
| DINP | 16.11 | 0.03 | 149 | 167 | 293 |
| DIDP | 17.44 | 0.03 | 149 | 167 | 307 |

Ionization energy of -70 eV in all cases.
Table S3.- Langmuir and Freundlich parameters of the adsorption isotherms of BBP onto the synthesized polymer.

|          | Langmuir | | Freundlich | | |
|----------|----------|---|------------|---|---|
|          | q_{max} (mg/g) | K_{L} (L/mg) | R^2    | K_{F} (L/m^2) | 1/n | R^2 |
| Langmuir | 579.86   | 0.17    | 0.9996   |
| Freundlich | 156.46  | 0.30    | 0.9243   |
Table S4.- Internal instrumental calibration data of the target analytes (DBP-d₄ was used as IS of BBP, DNPP-d₄ was used as IS of DIPP and DNPP, DHP-d₄ was used as IS of DHP, DEHA and DCHP, while DEHP-d₄ was used as IS of DEHP, DNOP, DINP and DIDP).

| Analytes | Studied linear range (µg/L) | Regression equation (n=8) | sₓ/x | R² | LOD (µg/L) | LOQ (µg/L) |
|----------|-----------------------------|---------------------------|------|----|------------|------------|
|          |                             | b ± sₓ·t₀.05;₆       | a ± sₓ·t₀.05;₆ |     |            |            |
| DIPP     | 0.5-150                     | 5.20·10⁻³ ± 2.40·10⁻⁴  | -1.34·10⁻² ± 1.79·10⁻² | 0.0156 | 0.9979     | 0.2        | 0.5        |
| DNPP     | 0.5-150                     | 9.82·10⁻³ ± 2.76·10⁻⁴  | -1.61·10⁻² ± 2.06·10⁻² | 0.0180 | 0.9992     | 0.2        | 0.5        |
| DHP      | 5-150                       | 1.14·10⁻² ± 4.92·10⁻⁴  | -3.88·10⁻² ± 4.24·10⁻² | 0.0245 | 0.9990     | 0.4        | 1.2        |
| BBP      | 5-150                       | 2.01·10⁻³ ± 2.00·10⁻⁴  | -1.39·10⁻² ± 1.72·10⁻² | 0.0100 | 0.9949     | 1.3        | 4.3        |
| DEHA     | 5-150                       | 2.93·10⁻³ ± 2.50·10⁻⁴  | -1.80·10⁻² ± 2.15·10⁻² | 0.0124 | 0.9962     | 0.7        | 2.5        |
| DCHP     | 5-150                       | 6.15·10⁻³ ± 3.61·10⁻⁴  | -3.02·10⁻² ± 3.11·10⁻² | 0.0180 | 0.9982     | 0.6        | 1.9        |
| DEHP     | 5-150                       | 9.46·10⁻³ ± 2.88·10⁻⁴  | -1.55·10⁻² ± 2.48·10⁻² | 0.0143 | 0.9995     | 0.2        | 0.7        |
| DNOP     | 5-150                       | 5.75·10⁻³ ± 3.16·10⁻⁴  | -5.72·10⁻⁴ ± 2.72·10⁻² | 0.0157 | 0.9984     | 1.3        | 4.4        |
| DINP     | 5-150                       | 3.88·10⁻³ ± 2.78·10⁻⁴  | 1.33·10⁻³ ± 2.40·10⁻² | 0.0139 | 0.9973     | 0.8        | 2.8        |
| DIDP     | 5-150                       | 2.82·10⁻³ ± 2.77·10⁻⁴  | 4.60·10⁻³ ± 2.38·10⁻² | 0.0138 | 0.9950     | 0.6        | 2.0        |
Table S5.- Relative recovery and RSD (between parenthesis) values of the target analytes in tap, waste and spring water (n=5 at each spiking level).

| Analytes | Sample       | Level 1<sup>a</sup> | Level 2<sup>a</sup> | Level 3<sup>a</sup> | Mean recovery value % (RSD) | LOQ<sub>method</sub> (ng/L) |
|----------|--------------|----------------------|----------------------|----------------------|-----------------------------|-----------------------------|
|          |              | Recovery % (RSD %)   | Recovery % (RSD %)   | Recovery % (RSD %)   |                             |                             |
| DIPP     | Tap water    | 116 (9)              | 113 (4)              | 107 (2)              | 112 (6)                     | 6.77                        |
|          | Wastewater   | 101 (4)              | 114 (6)              | 105 (6)              | 107 (7)                     | 10.2                        |
|          | Spring water | 120 (6)              | 113 (8)              | 116 (6)              | 116 (7)                     | 9.25                        |
| DNPP     | Tap water    | 99 (9)               | 101 (1)              | 97 (1)               | 99 (5)                      | 7.77                        |
|          | Wastewater   | 94 (4)               | 99 (8)               | 103 (3)              | 100 (7)                     | 11.0                        |
|          | Spring water | 109 (7)              | 95 (2)               | 100 (11)             | 101 (9)                     | 10.6                        |
| DHP      | Tap water    | 97 (3)               | 100 (2)              | 97 (2)               | 98 (2)                      | 15.6                        |
|          | Wastewater   | 95 (3)               | 106 (5)              | 106 (3)              | 102 (6)                     | 20.4                        |
|          | Spring water | 116 (7)              | 97 (6)               | 108 (7)              | 107 (10)                    | 21.1                        |
| BBP      | Tap water    | 115 (6)              | 109 (7)              | 106 (5)              | 110 (7)                     | 80.1                        |
|          | Wastewater   | 113 (9)              | 116 (11)             | 125 (7)              | 118 (10)                    | 139                         |
|          | Spring water | 119 (4)              | 83 (6)               | 120 (3)              | 107 (17)                    | 119                         |
| DEHA     | Tap water    | 98 (9)               | 120 (7)              | 106 (6)              | 108 (11)                    | 29.1                        |
|          | Wastewater   | 119 (6)              | 114 (6)              | 119 (2)              | 117 (5)                     | 36.0                        |
|          | Spring water | 127 (6)              | 104 (3)              | 114 (10)             | 115 (11)                    | 40.4                        |
| DCHP     | Tap water    | 92 (8)               | 99 (7)               | 88 (4)               | 93 (8)                      | 25.2                        |
|          | Wastewater   | 75 (10)              | 85 (11)              | 73 (16)              | 78 (14)                     | 41.5                        |
|          | Spring water | 102 (8)              | 96 (9)               | 111 (7)              | 103 (10)                    | 34.2                        |
| DEHP     | Tap water    | 77 (15)              | 63 (15)              | 99 (4)               | 80 (22)                     | 8.30                        |
|          | Wastewater   | 113 (9)              | 116 (8)              | 124 (8)              | 118 (9)                     | 7.26                        |
|          | Spring water | 101 (12)             | 132 (8)              | 79 (6)               | 102 (21)                    | 8.68                        |
Table S5.- (Continued).

| Analytes | Sample     | Level 1\(^a\) | Level 2\(^a\) | Level 3\(^a\) | Mean recovery value % (RSD) | LOQ\(_{\text{method}}\) (ng/L) |
|----------|------------|----------------|----------------|----------------|-----------------------------|-------------------------------|
|          |            | Recovery % (RSD %) | Recovery % (RSD %) | Recovery % (RSD %) |                             |                               |
| DNOP     | Tap water  | 101 (11)        | 100 (4)         | 93 (6)         | 98 (8)                      | 45.0                          |
|          | Wastewater | 93 (6)          | 91 (8)          | 104 (4)        | 96 (9)                      | 59.3                          |
|          | Spring water | 106 (5)        | 74 (5)          | 73 (8)         | 85 (20)                     | 68.8                          |
| DINP     | Tap water  | 118 (6)         | 105 (2)         | 99 (3)         | 107 (9)                     | 26.6                          |
|          | Wastewater | 109 (3)         | 112 (7)         | 114 (6)        | 112 (6)                     | 33.1                          |
|          | Spring water | 119 (5)       | 103 (5)         | 95 (4)         | 106 (11)                    | 35.9                          |
| DIDP     | Tap water  | 121 (2)         | 118 (4)         | 106 (6)        | 115 (7)                     | 17.4                          |
|          | Wastewater | 105 (3)         | 109 (8)         | 119 (7)        | 111 (8)                     | 23.3                          |
|          | Spring water | 114 (11)     | 98 (8)          | 98 (4)         | 103 (11)                    | 25.7                          |

\(^a\)Level 1 of 0.16 µg/L, level 2 of 0.6 µg/L and level 3 of 1.2 µg/L for all the analytes in the samples.
Table S6.- Matrix-matched calibration data of the target analytes in tap, waste and spring water (DBP-d₄ was used as IS of BBP, DNPP-d₄ was used as IS of DIBP, DIPP and DNPP, DHP-d₄ was used as IS of DHP, DEHA and DCHP, while DEHP-d₄ was used as IS of DEHP, DNOP, DINP and DIDP).

| Analytes | Sample      | Studied linear range (µg/L) | Regression equation (n=8) | Syx | R²    | ME (%)  |
|----------|-------------|-----------------------------|---------------------------|-----|-------|---------|
|          |             |                             | b ± s_b (10⁻⁵) | a ± s_a (10⁻⁵) |       |       |         |
| DIBP     | Tap water   | 0.5-150                     | 8.37·10⁻³ ± 3.56·10⁻⁴ | -8.50·10⁻³ ± 2.65·10⁻² | 2.32·10⁻² | 0.9982 | 61      |
|          | Wastewater  | 0.5-150                     | 8.40·10⁻³ ± 3.02·10⁻⁴ | -1.09·10⁻² ± 1.50·10⁻² | 1.31·10⁻² | 0.9994 | 62      |
|          | Spring water| 0.5-150                     | 8.15·10⁻³ ± 3.49·10⁻⁴ | -1.72·10⁻² ± 2.60·10⁻² | 2.27·10⁻² | 0.9982 | 57      |
| DINP     | Tap water   | 0.5-150                     | 1.25·10⁻² ± 3.77·10⁻⁴ | -2.03·10⁻² ± 2.81·10⁻² | 2.45·10⁻² | 0.9991 | 27      |
|          | Waste-water | 0.5-150                     | 1.27·10⁻² ± 3.47·10⁻⁴ | -2.15·10⁻² ± 2.59·10⁻² | 2.26·10⁻² | 0.9993 | 30      |
|          | Spring water| 0.5-150                     | 1.22·10⁻² ± 5.90·10⁻⁴ | -2.54·10⁻² ± 4.40·10⁻² | 3.84·10⁻² | 0.9977 | 25      |
| DHP      | Tap water   | 5-150                       | 1.39·10⁻² ± 3.86·10⁻⁴ | -3.35·10⁻² ± 3.32·10⁻² | 1.92·10⁻² | 0.9996 | 22      |
|          | Wastewater  | 5-150                       | 1.43·10⁻² ± 4.27·10⁻⁴ | -4.11·10⁻² ± 3.68·10⁻² | 2.13·10⁻² | 0.9995 | 25      |
|          | Spring water| 5-150                       | 1.38·10⁻² ± 5.75·10⁻⁴ | -2.72·10⁻² ± 4.95·10⁻² | 2.87·10⁻² | 0.9991 | 21      |
| BBP      | Tap water   | 5-150                       | 3.80·10⁻¹ ± 2.39·10⁻⁴ | -1.15·10⁻² ± 2.06·10⁻² | 1.19·10⁻² | 0.9979 | 89      |
|          | Wastewater  | 5-150                       | 4.29·10⁻¹ ± 1.47·10⁻⁴ | -1.98·10⁻² ± 1.26·10⁻² | 7.31·10⁻² | 0.9994 | 114     |
|          | Spring water| 5-150                       | 3.95·10⁻¹ ± 1.87·10⁻⁴ | -1.47·10⁻² ± 1.61·10⁻² | 9.30·10⁻³ | 0.9988 | 97      |
| DEHA     | Tap water   | 5-150                       | 4.90·10⁻₁ ± 2.59·10⁻⁴ | -1.23·10⁻² ± 2.23·10⁻² | 1.29·10⁻² | 0.9986 | 68      |
|          | Wastewater  | 5-150                       | 5.19·10⁻¹ ± 3.18·10⁻⁴ | -2.00·10⁻² ± 2.74·10⁻² | 1.59·10⁻² | 0.9981 | 77      |
|          | Spring water| 5-150                       | 4.75·10⁻¹ ± 2.05·10⁻⁴ | -1.56·10⁻² ± 1.77·10⁻² | 1.02·10⁻² | 0.9990 | 62      |
| DCHP     | Tap water   | 5-150                       | 8.61·10⁻³ ± 4.02·10⁻⁴ | -3.34·10⁻² ± 3.46·10⁻² | 2.00·10⁻² | 0.9989 | 40      |
|          | Waste-water | 5-150                       | 7.21·10⁻³ ± 2.88·10⁻⁴ | -2.22·10⁻² ± 2.48·10⁻² | 1.43·10⁻² | 0.9992 | 17      |
|          | Spring water| 5-150                       | 7.61·10⁻³ ± 4.65·10⁻⁴ | -1.87·10⁻² ± 4.01·10⁻² | 2.32·10⁻² | 0.9981 | 24      |
| DEHP     | Tap water   | 5-150                       | 1.24·10⁻² ± 7.54·10⁻⁴ | 4.63·10⁻³ ± 6.49·10⁻² | 3.76·10⁻² | 0.9981 | 31      |
|          | Wastewater  | 5-150                       | 1.54·10⁻² ± 8.43·10⁻⁴ | 4.29·10⁻³ ± 7.26·10⁻² | 4.20·10⁻² | 0.9985 | 63      |
|          | Spring water| 5-150                       | 1.13·10⁻² ± 7.69·10⁻⁴ | 5.58·10⁻³ ± 6.62·10⁻² | 3.83·10⁻² | 0.9976 | 19      |
| DNOP     | Tap water   | 5-150                       | 1.84·10⁻² ± 1.37·10⁻³ | -1.08·10⁻² ± 1.18·10⁻¹ | 6.84·10⁻² | 0.9971 | 219     |
|          | Wastewater  | 5-150                       | 1.92·10⁻² ± 9.71·10⁻⁴ | -9.91·10⁻³ ± 8.36·10⁻² | 4.84·10⁻² | 0.9987 | 234     |
|          | Spring water| 5-150                       | 1.82·10⁻² ± 1.37·10⁻³ | -1.02·10⁻² ± 1.18·10⁻¹ | 6.81·10⁻² | 0.9971 | 217     |
Table S6.- Continued.

| Analytes | Sample     | Studied linear range (µg/L) | Regression equation (n=8) | $s_y/x$ | $R^2$ | ME (%)* |
|----------|------------|-----------------------------|---------------------------|---------|-------|---------|
|          |            |                             | $b \pm s_b t_{(0.05,6)}$ | $a \pm s_a t_{(0.05,6)}$ |       |        |         |
| DINP     | Tap water  | 5-150                       | $1.72 \cdot 10^{-2} \pm 6.58 \cdot 10^{-4}$ | $1.92 \cdot 10^{-2} \pm 5.67 \cdot 10^{-2}$ | $3.28 \cdot 10^{-2}$ | 0.9992 | 343     |
|          | Wast-water | 5-150                       | $1.91 \cdot 10^{-2} \pm 4.34 \cdot 10^{-4}$ | $-9.25 \cdot 10^{-3} \pm 3.73 \cdot 10^{-2}$ | $2.16 \cdot 10^{-2}$ | 0.9997 | 394     |
|          | Spring water | 5-150                  | $1.58 \cdot 10^{-2} \pm 1.43 \cdot 10^{-3}$ | $5.25 \cdot 10^{-3} \pm 1.23 \cdot 10^{-1}$ | $7.14 \cdot 10^{-2}$ | 0.9957 | 307     |
| DIDP     | Tap water  | 5-150                       | $1.37 \cdot 10^{-2} \pm 7.80 \cdot 10^{-4}$ | $-5.86 \cdot 10^{-2} \pm 6.72 \cdot 10^{-2}$ | $3.89 \cdot 10^{-2}$ | 0.9983 | 387     |
|          | Wastewater | 5-150                       | $1.62 \cdot 10^{-2} \pm 8.65 \cdot 10^{-4}$ | $-8.63 \cdot 10^{-2} \pm 7.45 \cdot 10^{-2}$ | $4.31 \cdot 10^{-2}$ | 0.9985 | 473     |
|          | Spring water | 5-150                  | $1.31 \cdot 10^{-2} \pm 6.72 \cdot 10^{-4}$ | $-5.65 \cdot 10^{-2} \pm 5.79 \cdot 10^{-2}$ | $3.35 \cdot 10^{-2}$ | 0.9986 | 363     |
Table S7.- pH and conductivity data of the water samples analyzed in this work.

|               | pH   | Conductivity (µS/cm) at 25 ºC |
|---------------|------|-------------------------------|
| **Tap water** |      |                               |
| Sample 1      | 9.07 | 999                           |
| Sample 2      | 8.65 | 1030                          |
| Sample 3      | 9.03 | 595                           |
| Sample 4      | 7.77 | 641                           |
| **Wastewater**|      |                               |
| Sample 1      | 8.69 | 1723                          |
| Sample 2      | 8.54 | 1360                          |
| Sample 3      | 7.85 | 1159                          |
| Sample 4      | 7.91 | 556                           |
| Sample 5      | 8.38 | 1440                          |
| Sample 6      | 8.51 | 1898                          |
| **Spring water** |    |                               |
| Sample 1      | 9.34 | 1775                          |
| Sample 2      | 8.53 | 801                           |

Sample 1 was also used for validation purpose.
Table S8.- Previous studies in which a dSPE procedure has been applied for the extraction of plasticizers from water samples.

| Analytes                        | Sorbent (amount) | Matrix (volume)                                                                 | Extraction technique | Separation and detection technique | Recovery % (RSD %) | LODs | Comments                                                                                                                                                                                                                                                                                                                                 | Reference                                      |
|---------------------------------|------------------|-------------------------------------------------------------------------------|---------------------|------------------------------------|--------------------|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|
| DIBP, DBP, DEHA, DIOP           | MOF-70 (17 mg)   | Mineral water, carbonated soft drink, injection serum and sterile distilled water (5 mL) | µdSPE               | GC-FID                             | 40-68% (2-5%)      | 880-1040 ng/L | 2-propanol was used as the desorption solvent. The final supernatant collected at µ-dSPE was used as a disperser solvent in the next DLLME procedure.                                                                                                                                   | Pezhhanfar et al., *J. Food Compos. Anal.* 2021, 104, 104174. |
| DMP, DEP, DIBP, DBP, DMEP, BMPP, DEEP, DNPP, DHP, BBP, DBEP, DCHP, DEHP, DNOP, DNP | Graphene (3 mL, 1.5 mg/mL) | River and sea water (20 mL) | dSPE | GC-MS | 71-117% (1-10%) | 2000-6000 ng/L | TPP was used as IS. Colloidal graphene at a concentration of 1.5 mg/mL was prepared via chemical reduction of exfoliated GO. EtOAc was used as desorption solvent.                                                                 | Wu et al., *Sci. Total Environ.* 2013, 444, 224-230. |
| DEHP                            | GO-MIPs (20 mg)  | River, lake and rain water (600 mL)                                          | µdSPE               | HPLC-UV                            | 82-92% (< 6.7%)    | 920 ng/L | Acetone was used as elution solvent.                                                                                                                                                                                                                                                                                                  | Cheng et al., *J. Chromatogr. A* 2017, 1511, 85-91. |
| BBP, DBEP, DIPP, DNPP, DEHA, DCHP, DEHP, DNOP, DINP | Basolite® F300 (120 mg) | Tap, pond and waste water (50 mL) | dSPE | HPLC-MS                           | 70-118% (1-19%)  | 6.6-20.7 ng/L | DHP-d$_4$ was used as IS. ACN was used as elution solvent. A small signal                                                                                                                                                                                                     | González-Sálamo et al., *Talanta* 2019, 195, 236-244. |
| Solvent          | Extraction solvent | Method      | Concentration | Comments                                                                 |
|------------------|--------------------|-------------|---------------|--------------------------------------------------------------------------|
| Bottled mineral water (100 mL) | μdSPE, LC-MS       | 56-125% (0-22%) | 1.6-23.2 ng/L | Five different sorbents were tested. MeOH was used as the extraction solvent. Vivas et al., Food Chem. 2022, 370, 131062. |
| Bottled mineral water and boiling water kept in plastic containers (75 mL) | μdSPE, GC-FID     | 88-110% (4-8%) | 200-700 ng/L | EtOAc was used as elution solvent. Tahmasebi et al., RSC Adv. 2016, 6, 40211-40218. |
| Drinking water and distilled herbal beverages (10 mL) | μdSPE, GC-MS       | 55-113% (0-10%) | 60-300 ng/L | BnBzO was used as IS. Ace:MeOH (80:20, v/v) was used as elution solvent. The sorbent could be used for at least 4 times. Otoukesh et al., J. Chromatogr. A 2020, 1625, 461307. |
| Plastic bottled water and artificial saliva (200 mL) | μdSPE, GC-MS       | - (-)       | 310-410 ng/L | BnBzO was used as IS. DCM was used as elution solvent. Özer et al., J. Chromatogr. A 2017, 1500, 53-60. |
| Tap, waste and spring water | μdSPE, GC-MS       | 63-132% (1-16%) | 2.03-41.6 ng/L | Four ISs were used. EtOAc was used as elution solvent. This work |
μdSPE: micro dispersive solid-phase extraction; 4-NP: 4-nonylphenol; 4-OP: 4-octylphenol; 4-tOP: 4-tert-octylphenol; Ace: acetone; ACN: acetonitrile; BBP: benzyl butyl phthalate; BMPP: bis(4-methyl-2-pentyl) phthalate; BnBzO: benzyl benzoate; BPA: bisphenol A; DBEP: bis(2-butoxyethyl) phthalate; DBP: dibutyl phthalate; DCHP: dicyclohexyl phthalate; DCM: dichloromethane; DEEP: bis(2-ethoxyethyl) phthalate; DEHA: di(2-ethylhexyl) adipate; DEHP: di(2-ethylhexyl) phthalate; DEP: diethyl phthalate; DHP: dihexyl phthalate; DHP-d4: dihexyl phthalate-3,4,5,6-d4; DIBP: diisobutyl phthalate; DIDP: diisodecyl phthalate; DINP: diisononyl phthalate; DIOP: diisooctyl phthalate; DIPP: diisopentyl phthalate; DLLME: dispersive liquid-liquid microextraction; DMEP: bis(2-methoxyethyl) phthalate; DMIM: dummy molecularly imprinted microbead; DMP: dimethyl phthalate; DNOP: di-n-octyl phthalate; DNP: dinonyl phthalate; DNPP: di-n-pentyl phthalate; DOA: dioctyladipate; dSPE: dispersive solid-phase extraction; E1: estrone; E2: 17β-estradiol; E3: estriol; EE2: 17α-ethinylestradiol; EtOAc: ethyl acetate; FID: flame ionization detection; GC: gas chromatography; GO: graphene oxide; HPLC: high-performance liquid chromatography; IS: internal standard; LC: liquid chromatography; LDH: layered double hydroxide; LOD: limit of detection; MeOH: methanol; MIP: molecularly imprinted polymer; MOF: metal organic framework; MS: mass spectrometry; PEMATrp: poly(ethylene glycol dimethacrylate N-methacryloyl-L-tryptophan methyl ester); RSD: relative standard deviation; SPAN: sulfonated polyaniline; TPP: triphenyl phosphate; UV: ultraviolet.
POLYMER SYNTHESIS

Compound (2): trimethyl benzene-1,3,5-tricarboxylate
Trimesic acid (1) (3.00 g, 14.3 mmol) was dissolved in 60 mL of MeOH. H₂SO₄ was slowly added (0.75 mL) and the reaction was refluxed for 24 h before being allowed to cool to r.t. An aqueous NaHCO₃ solution (saturated) was slowly added to neutralize the mixture. The aqueous phase was extracted with Et₂O (3x20 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. Compound 2 was obtained as a white solid in quantitative yield.

¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm): 8.86 (s, 3H), 3.98 ppm (s, 9H).
¹³C NMR (150 MHz, CDCl₃, 298 K) δ (ppm): 165.58, 134.75, 131.37, 52.78.
HRMS (EI-TOF): m/z: calc for C₁₂H₁₂O₆ [M⁺]: 252.0634, found: 252.0639.

Compound (4): 1,3,5-tris(bromomethyl)benzene
According to the literature, triester 2 (3.6 g, 14.3 mmol) was dissolved in THF (75 mL) and it was added dropwise over a solution of LiAlH₄ (2.56 g, 64.4 mmol) in THF at 0 °C. The reaction was refluxed during 24 h before being allowed to cool. Upon cooling, H₂O was carefully added (50 mL) and the mixture was filtered through a celite pad, and the filter cake was washed with DCM. The volatiles were concentrated under reduced pressure. After that, the crude of alcohol 3 was mixed with 20.9 mL of HBr in HAc solution (33% w/v) and stirred over night to obtain a needle-like off-white solid that was filtered, generously washed with water and dried under reduced pressure. 4.03 g, 79% yield.

¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm): 7.34 (s, 3H), 4.46 ppm (s, 6H).
¹³C NMR (150 MHz, CDCl₃, 298 K) δ (ppm): 139.21, 129.72, 32.31.
HRMS (EI-TOF): m/z: calc for C₉H₉Br₃ [M⁺]: 359.8193, found: 359.8217; calc for C₉H₉Br₃ [M⁺]: 353.8254, found: 353.8262

Compound (5): 1,3,5-tris(bromomethyl)-2-nitrobenzene
A mixture of HNO₃ (27 mL) and H₂SO₄ (31 mL) in a round bottom flask was cooled down in an ice-water bath. Compound 4 (11.5 g, 32.2 mmol) was carefully added in a period of 10 min keeping the temperature at 0 °C for 1 h after the complete addition. The mixture was allowed to reach room temperature and an ice-water mixture was added. The aqueous phase was extracted with DCM (3x50 mL), and the organic layer was washed with H₂O (3x40 mL), dried over MgSO₄, filtered and concentrated under reduce pressure. Compound 5 was obtained as a white solid after purification by column chromatography on silica gel (AcOEt/Hex 5:95). 9.83 g, 76% yield.
$^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): 7.52 (s, 2H), 4.48 (s, 4H), 4.45 ppm (s, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): 141.75, 132.28, 131.8, 30.33, 26.27.

HRMS (EI-TOF): m/z: calc for C$_9$H$_8$NO$_2$Br$_3$ [M+]: 404.8044, found: 404.8058; calc for C$_9$H$_8$NO$_2$Br$_3$ [M+]: 398.8105, found: 398.8110

Polymer Synthesis:

NO$_2$-polymer: compound 5 (0.84 g, 3.9 mmol), K$_2$CO$_3$ (1.25 g, 9.1 mmol) and commercially available 6 (1.04 g, 2.6 mmol) were placed in a round bottom flask under N$_2$ atmosphere with a magnetic stirrer. Dry DMF (13 mL, 0.2M) was added and the solution was heated for 18 h at 80 °C. The mixture was cooled to room temperature and 20 mL of Milli-Q H$_2$O were added appearing a white solid. The mixture was let to stir for 1 additional hour and the solid was filtered, washed with Milli-Q H$_2$O (2x20 mL), MeOH HPLC grade (2x15 mL) and ACN HPLC grade (2x15 mL). Finally, the white solid was dried in high vacuum. 1.17 g, 93% yield.

Before use, if necessary, the polymer was washed with an appropriate volume of different organic solvents (i.e., ACN, MeOH or AcOEt) to remove any impurities or plasticizers. Then, it was dried under vacuum and acidified with a 0.1 M HCl solution and subsequently washed with Milli-Q water until neutral pH. Finally, it was completely dried under vacuum.
DEGRADATION STUDIES

Photodegradation:

1.4 mg of the polymer (2.89 mmol) was added to a quartz NMR tube, followed by 0.17 mL of a 0.0145 M solution of hexamethyldisilane in DMSO-D$_6$ (as IS). The volume of the tube was adjusted to 0.7 mL and exposed to UV light with an ACE-Hanovia photochemical lamp 7830-60 (450W) and monitored by $^1$H-NMR experiment.

To obtain the concentration of the carboxylic acid, 1 peak of IS and 1 signal of the acid were deconvolutionated to obtain the areas. With those values, a quotient of both was done to obtain the concentration.

IS: Internal Standard

$$0.0145 \text{ M of IS} = \frac{x \text{ mmol}}{0.17 \text{ mL}} \rightarrow 0.00246 \text{ mmol} \quad \text{0.7 mL} \rightarrow 0.0035 \text{ M of IS}$$

$$\text{Acid (M)} = \frac{\text{Area of acid}}{\text{Area of IS}} \div \text{ConcIS}$$
| Time (min) | Area of IS | Area of acid | Conc (M)       |
|-----------|------------|--------------|---------------|
| 30        | 4.819·10^7 | 2.286·10^9  | 1.67·10^-3   |
| 60        | 5.628·10^{12} | 6.575·10^{10} | 4.11·10^-3   |
| 90        | 5.942·10^{12} | 1.166·10^{11} | 6.91·10^-5   |
| 120       | 5.339·10^{12} | 1.359·10^{11} | 8.97·10^-5   |
| 150       | 4.545·10^{12} | 1.494·10^{11} | 1.16·10^-4   |
| 210       | 5.471·10^{12} | 2.113·10^{11} | 1.36·10^-4   |
| 255       | 4.211·10^{12} | 1.622·10^{11} | 1.36·10^-4   |
| 355       | 4.077·10^{12} | 1.577·10^{11} | 1.36·10^-4   |
Self-immolation:

1.2 mg of the polymer (2.48 mmol) was added to a NMR tube, followed by 0.17 mL of a 0.0145 M solution of hexamethyldisilane in DMSO-D$_6$ (as internal standard). The volume of the tube was adjusted to 0.7 mL by adding DMSO-D$_6$ (0.33 mL) and a saturated D$_2$O solution of Na$_2$S$_2$O$_4$ (0.2 mL) and heated to 100 ºC in an oil bath. The process was monitored by $^1$H-NMR experiment.
Self-immolation NMR is cleaner than the photodegradation because the latter only break one of the three links to the central node, and therefore several soluble oligomers are expected, which yields a messier spectrum with wide signals combined with sharp ones. Self-immolation however, leads to a theoretically complete degradation.
DEGRADATION-REPOLYMERIZATION CYCLE STUDY

A reductive degradation with sodium dithionite (335 mg) starting from 100 mg of polymer CSP-1 in 20 mL of acetone:water (9:1, v/v) was carried out. After 12 h of reflux, the polymer was degraded. The reaction was cooled down to room temperature, and the solvents were evaporated and the solid was vacuum dried. A portion of such crude residue was dissolved in DMF and 27 mg of 1,3,5-tris(bromomethyl)-2-nitrobenzene (TBMNB) and 32 mg of K₂CO₃ were added to the reaction flask and the reaction was performed as explained before.

A white polymer was obtained, which gives an IR spectrum that matched that of the original polymer, confirming that the crude mixture obtained after the degradation can be used for repolymerization of CSP-1.
Figure S1.- FTIR spectra of NDCA, TBMNB and the CSP-1.
Figure S2.- FTIR spectra of the CSP-1 synthesized in different batches.
Figure S3.- X-ray diffraction pattern obtained for the polymer showing the shape of a predominantly amorphous material.
Figure S4.- TGA curve of the CSP-1.
Figure S5.- $N_2$ adsorption isotherm plot of the CSP-1.
Figure S6.- SEM images of the CSP-1.
Figure S7.- Photograph of the resulting mixtures of 40 mg of the polymer and 5 mL of water at pH 11, 12, 13 and 14.
Figure S8.- BBP HPLC-UV calibration curve (top) and adsorption isotherm of BBP onto CSP-1 (down).
Figure S9.- Effect of the pH during the extraction step on the peak areas of the target PAEs. Extraction conditions: 30 mg sorbent, 50 mL of spiked Milli-Q water at 125 μg/L, manual agitated for 2.5 min and elution with 15 mL of ethyl acetate.
Figure S10.- Effect of the sorbent amount used in the extraction step on the peak areas of the selected PAEs. Extraction conditions: 50 mL of spiked Milli-Q water at 125 μg/L (pH 4.0), manual agitated for 2.5 min, and elution with 15 mL of ethyl acetate.
Figure S11.- Effect of the solvent used in the elution step on the peak areas of the selected analytes. Extraction conditions: 30 mg sorbent, 50 mL of spiked Milli-Q water at 125 µg/L (pH 6.0), manual agitated for 2.5 min, and elution with 15 mL of each solvent.