

Natural Eutectic Solvents for Recycling of Poly(ethyleneterephthalate): Closing the Circle

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Supporting Information

DES preparation

Table S1. lists the chemical compounds used in the Eutectic Solvents (ES) preparation and the chemical structures are presented in Fig. S1. These compounds were used as received. The ES prepared in this work have the molar ratio of 1:1. This ratio was taken from literature^{52,53} to guarantee that liquid phase was attained at room temperature. The ES were prepared carefully weighed, using an analytical high-precision balance Mettler Toledo scale (New Classic MS205DU) with an uncertainty of $\pm 10^{-4}$ g, and then slowly heated up with constant stirring, using a heating-stirring plate (Heidolph, MR Hei-Tec), until a clear liquid phase was observed. The heat was turned off and the mixtures were allowed to slowly to cool down to room temperature.

Table S1 Chemical Name, Acronym, CAS Registry Number, Mass Fraction Purity, and Chemical Source of the chemical compounds used in ES preparation.

Chemical Name	Acronym	CAS Reg. No	Source	Mass Fraction Purity
Choline Chloride	ChCl	67-48-1	Alfa Aesar	0.98
Tetrabutyl ammonium chloride	N4444Cl	1112-67-0	Acros Organics	0.95
Tetraoctyl ammonium bromide	N8888Br	1486-33-2	Acros Organics	0.98
Trioctylmethyl ammonium bromide	N8881Br	35675-80-0	Sigma Aldrich	0.97
Acetic Acid	-	64-19-7	Sigma Aldrich	0.997
Propionic Acid	-	79-09-4	Sigma Aldrich	0.995
Decanoic Acid	-	334-48-5	Alfa Aesar	0.99
Dodecanoic Acid	-	143-07-7	Sigma Aldrich	0.98
Phenylacetic Acid	-	103-82-2	Sigma Aldrich	0.99
Methanesulfonic Acid	-	75-75-2	Sigma Aldrich	0.995
Citric Acid	-	77-92-9	Sigma Aldrich	0.995
p-Toluene Sulfonic Acid	-	6192-52-5	Acros organics	0.99
Ethylene Glycol	-	107-21-1	Carlo Erba	0.995
Glycerol	-	56-81-5	Sigma Aldrich	0.99
Urea	-	57-13-6	Sigma Aldrich	0.99

Thymol	-	89-83-8	Sigma Aldrich	0.99
Carvacrol	-	499-75-2	TCI	0.98
DL-Menthol	-	89-78-1	Sigma Aldrich	0.95

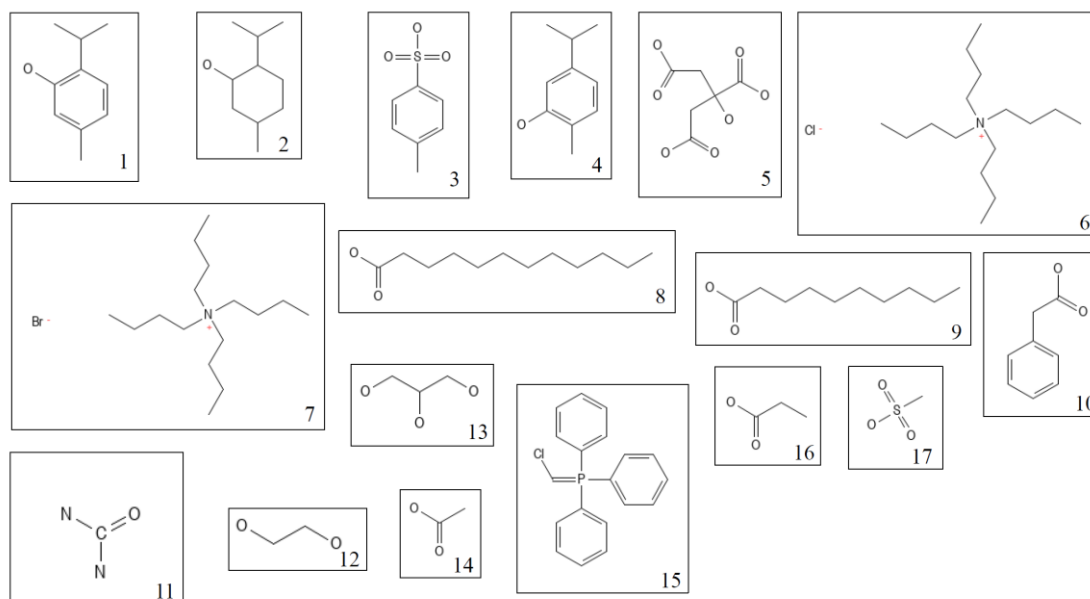


Fig. S1 Chemical structures of the compounds used to prepare the ES used in this work. 1) Thymol; 2) DL-Menthol; 3) p-Toluenesulfonic Acid; 4) Carvacrol; 5) Citric Acid; 6) N4444Cl; 7) N8888Br; 8) Dodecanoic Acid; 9) Decanoic Acid; 10) Phenylacetic Acid; 11) Urea; 12) Ethyleneglicol; 13) Glycerol; 14) Acetic Acid; 15) ChCl; 16) Propionic Acid; 17) Methanesulfonic Acid.

Eutectic Solvent Screening

PET from a water (LUSO) bottle was cut in small discs of 0.5 cm of diameter with a mould. The solubility of PET in the selected ES was determined by inserting PET and ES in a vial, in a mass ratio 1/10, which was placed in silicone bath for 6 hours at 100°C, or 150°C, or both depending on the decomposition temperature of each DES. After the period of 6 hours, the PET discs that did not solubilize were removed from the solvent, washed with water, dried in an oven at 40°C, and weighed in a high-precision balance Mettler Toledo scale (New Classic MS205DU) until a constant mass was obtained. The percentage of mass uptake ($\%m_{\text{uptake}}$), due to solvent swelling, was calculated using the following equation

$$\%m_{\text{uptake}} = \frac{(m_{\text{PET}}^{\text{initial}} - m_{\text{PET}}^{\text{final}})}{m_{\text{PET}}^{\text{initial}}} \times 100 \quad (\text{E1})$$

where $m_{PET_{initial}}$ and $m_{PET_{final}}$ are the initial mass of PET and that after contact with ES. The results for $\%m_{uptake}$ for the studied ES are presented in Fig. S2 at 100°C and 150°C. The screening was initially conducted at 100°C for several ES, but small values of $\%m_{uptake}$ were observed, indicating the low solubility of PET in these solvents. The exception is the thymol:carvacrol ES, where a $\%m_{uptake}$ of 45.6% at 100°C was registered.

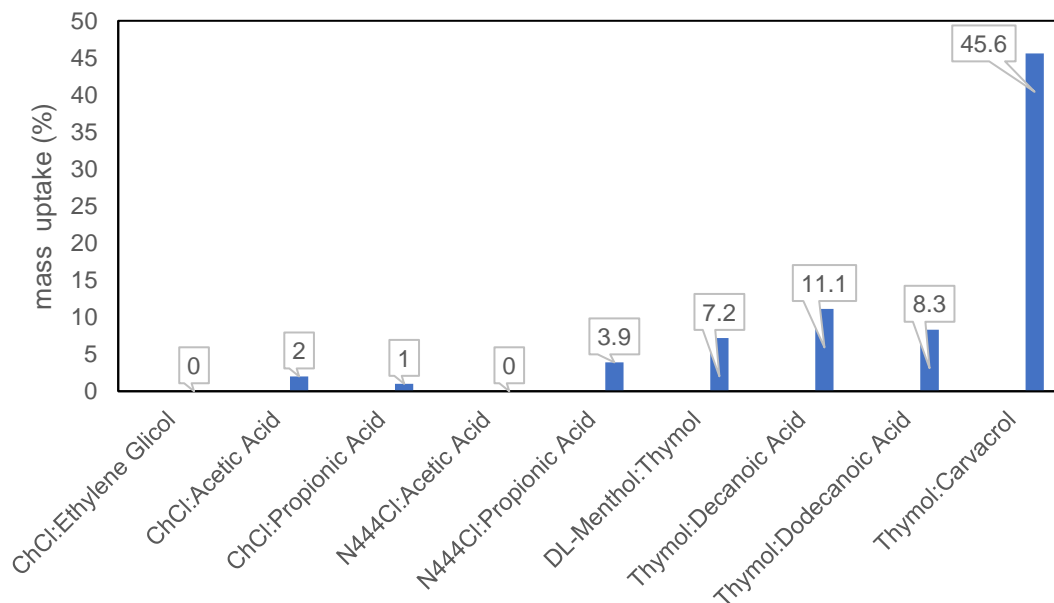


Fig. S2 Percentage of PET mass uptake for each ES at 100°C.

To evaluate the possibility of full dissolution of PET in this ES, a study of PET solubility was carried out at different temperatures up to 150°C. It was observed a $\%m_{uptake}$ of 46.3% and 62.1% for the temperatures of 110°C and 120°C. However, at 130°C the full dissolution of PET was observed, after swelling and burst out of all disks. Table S1 shows the study of the time required for PET dissolution in thymol:carvacrol (1.1), at a PET / ES ratio of 1/10, as a function of temperature.

Table S2. Time required for PET dissolution in thymol:carvacrol (1.1), at a PET / ES ratio of 1/10, as a function of temperature.

Temperature/°C	time/min
130	23
140	20
150	7

Taking into account these results, other ES were also selected to carry out the screening at 150°C, depending on their decomposition temperature. However, the results in Fig. S3 show low swelling values (bellow or equal to 10% in mass) for all the tested ES.

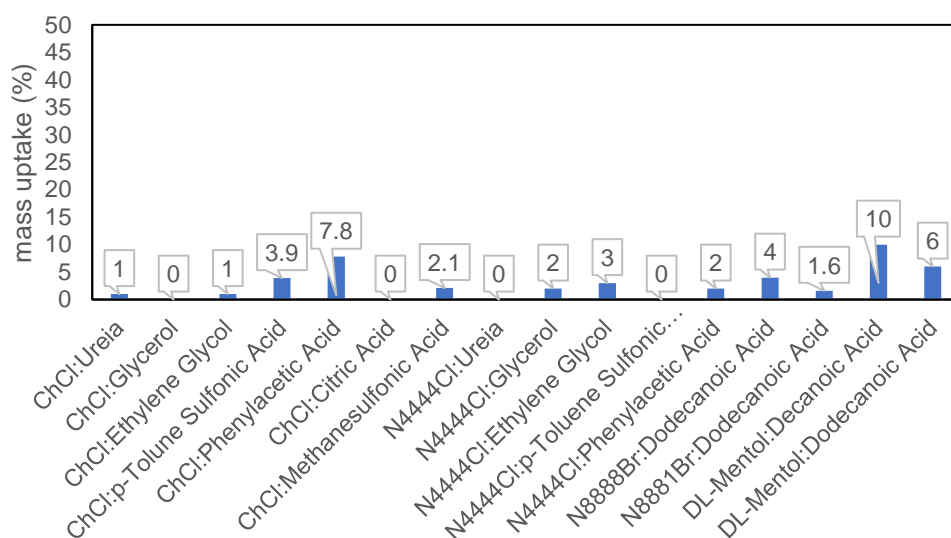


Fig. S3 Percentage of PET mass uptake for each ES at 150°C.

To study the solubility of PET at 150°C, different PET/ES ratios were selected. All the studied ratios were fully soluble at 150°C, and the only difference observed was the amount of time taken to achieve full solubilization. These results are shown the Fig. S4.

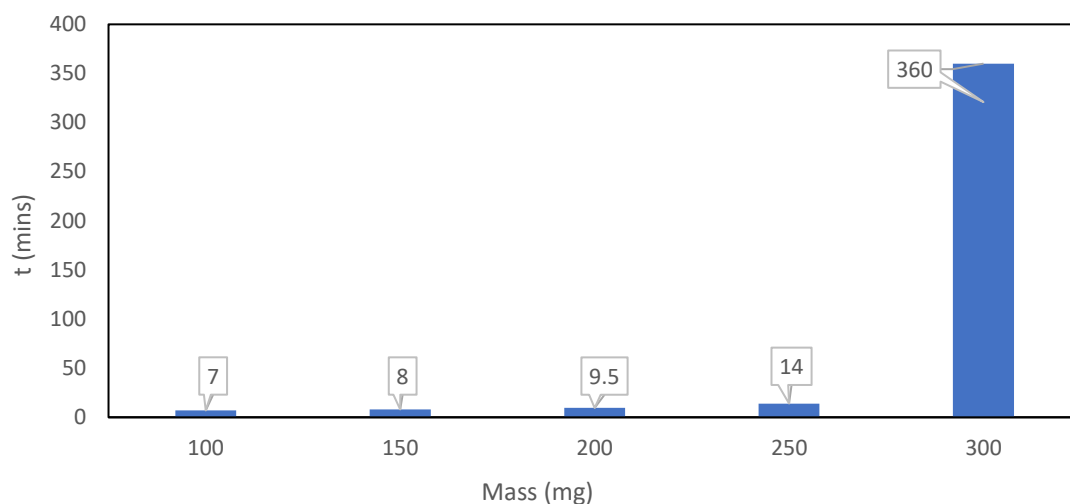


Fig. S4 Time required for full solubilization of PET at different PET/ES ratios at 150°C. The mass of ES used was 1 g.

At a PET/ES ratio of 3:10 (300 mg PET), a great increase in the time for solubilization, almost 3h, was observed. This is in contrast with other samples where lower amounts of PET were used. However, as it can be seen in Fig. S5, after cooling down to room temperature, all solutions became turbid due to PET precipitation, except for that where PET/ES ratio of 1/10 (100 mg PET) was used.



Fig. S5 PET in thymol:carvacrol (1:1) samples at room temperature, after full PET solubilization at 150°C. PET/ES ratio from left to right 1:10, 2:10, 3:10.

PET precipitation

PET was precipitated from thymol:carvacrol (1:1) ES through the addition of ethanol/water mixtures with different compositions. PET was filtered from the final solutions, washed with water, dried in an oven at 40°C, and weighed in a high-precision balance Mettler Toledo scale (New Classic MS205DU). In order to get all the thymol:carvacrol (1:1) out of PET, PET was frozen using liquid nitrogen and grinded and dried again in the oven. This procedure was repeated until a constant mass was obtained. The percentage of PET recovered was calculated as follows:

$$\% PET_{recovered} = \frac{(mPET_{initial} - mPET_{precipitated})}{mPET_{initial}} \times 100 \quad (E2)$$

Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) Spectroscopy

In the present work, the Fourier Transform Infrared samples characterization was carried in the mid-IR (4000-450 cm^{-1}) to study the fundamental vibrations and associated rotational-vibrational structure using a PerkinElmer Spectrum Two FTIR Spectrometer with a diamond crystal. Each FTIR spectrum presented was based on a recording of 16 scans at a resolution of 4 cm^{-1} . The ATR crystal was carefully cleaned with ethanol between measurements. In order to identify functional groups and the related compound class, for each relevant peak, a IR spectrum table¹⁰⁸ was used, along with reported FTIR spectra of known compounds^{109 110}.

In Fig. S6 the ATR-FTIR spectra of virgin PET and precipitated PET using 40(v/v)% water and ethanol mixture are compared. In Fig. S7 ATR-FTIR spectra of swollen virgin PET in several ES, thymol:carvacrol (1:1) in thymol:decanoic acid (1:1) DL-menthol:decanoic acid (1:1), are compared.

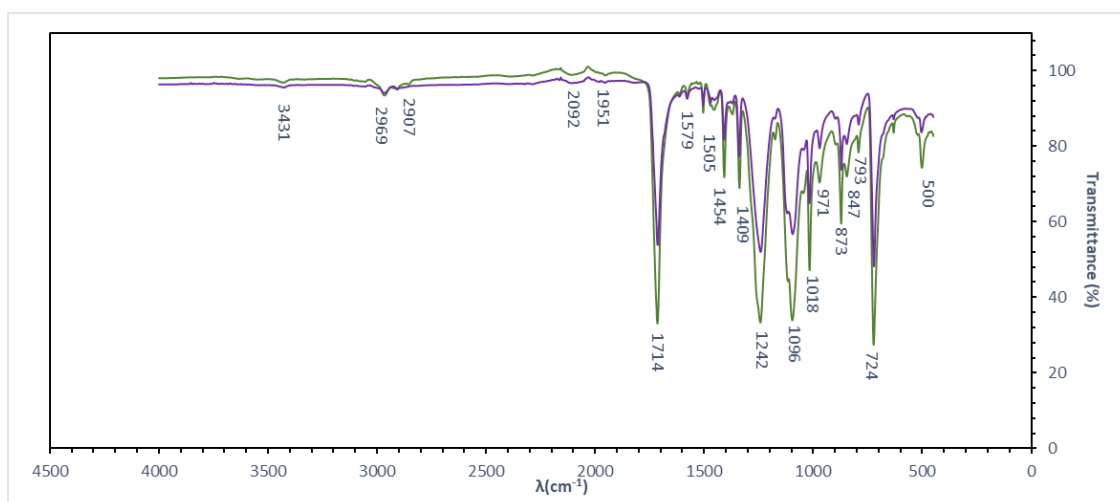


Fig. S6 ATR-FTIR spectra of virgin PET (green) and precipitated PET (purple) using 40(v/v)% water and ethanol mixture.

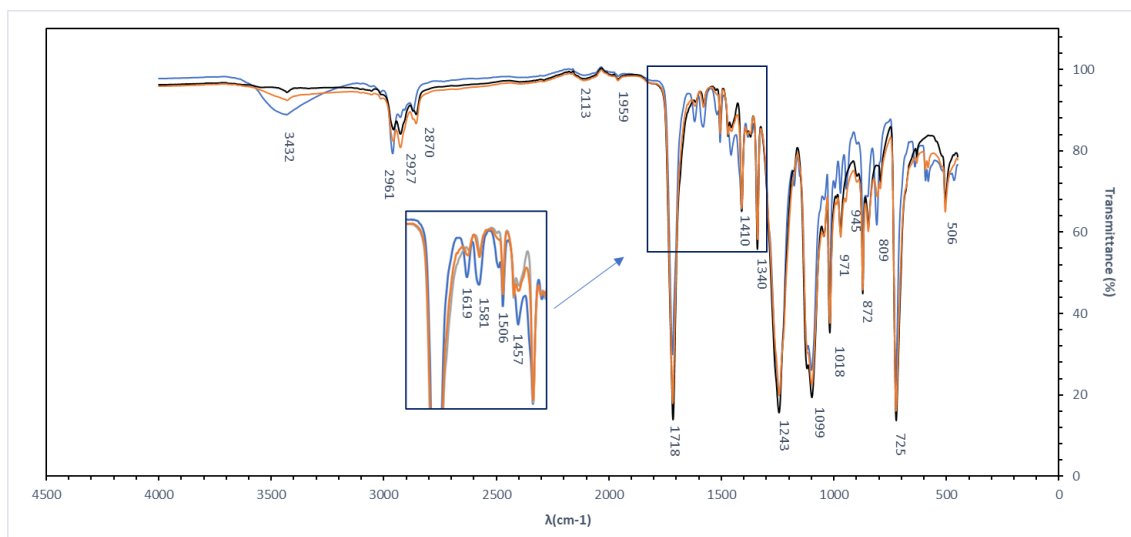


Fig. S7 ATR-FTIR spectra of swollen virgin PET in thymol:carvacrol (1:1) (blue), in thymol:decanoic acid (1:1) (orange), DL-menthol:decanoic acid (1:1) (black).

Differential Scanning Calorimetry (DSC)

A NETZSCH Differential Scanning Calorimeter model 200F3 was used in this work. Samples of approximately 10 mg were weighed into a pan, that was closed using a pressing machine. Once inside the DSC, the pans along with the reference pan were heated and cooled between -70°C to 290°C performing three heating-cooling cycles, at $10^{\circ}\text{C}/\text{min}$. The first two heating-cooling cycles were done to clean any impurity inside the sample pan and to clean the polymer thermal history and only the last cycle was analyzed. A nitrogen (N_2) flow rate, at $50\text{ ml}/\text{min}$, was used to create an inert atmosphere and also to promote a good heat conductivity.

In Fig. S8 and S9 the thermal transitions of virgin PET and precipitated PET sample using 40 (v/v)% water and ethanol mixture are presented, respectively.

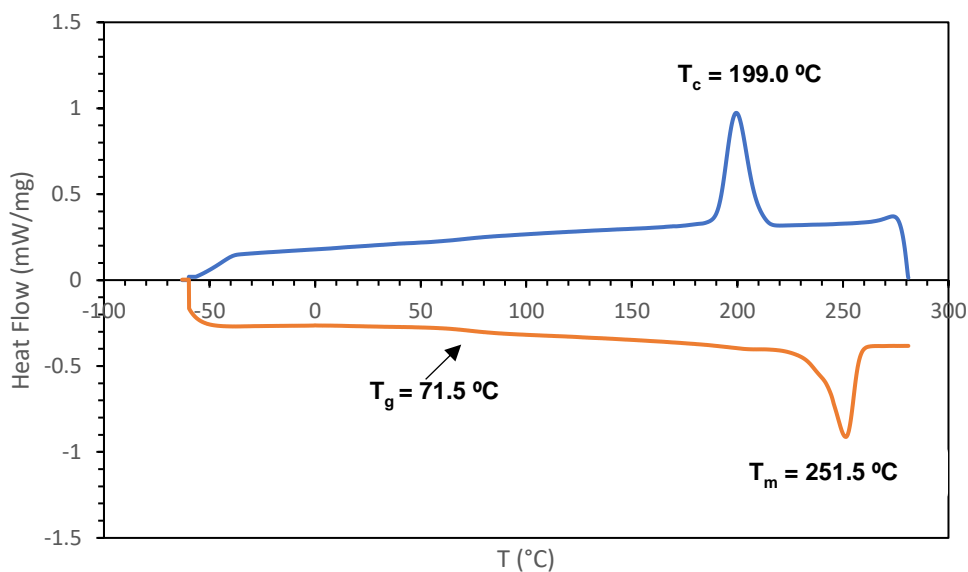


Fig. S8 Thermal transitions of virgin PET sample. Blue line denotes cooling cycle, while green line denotes the heating cycle.

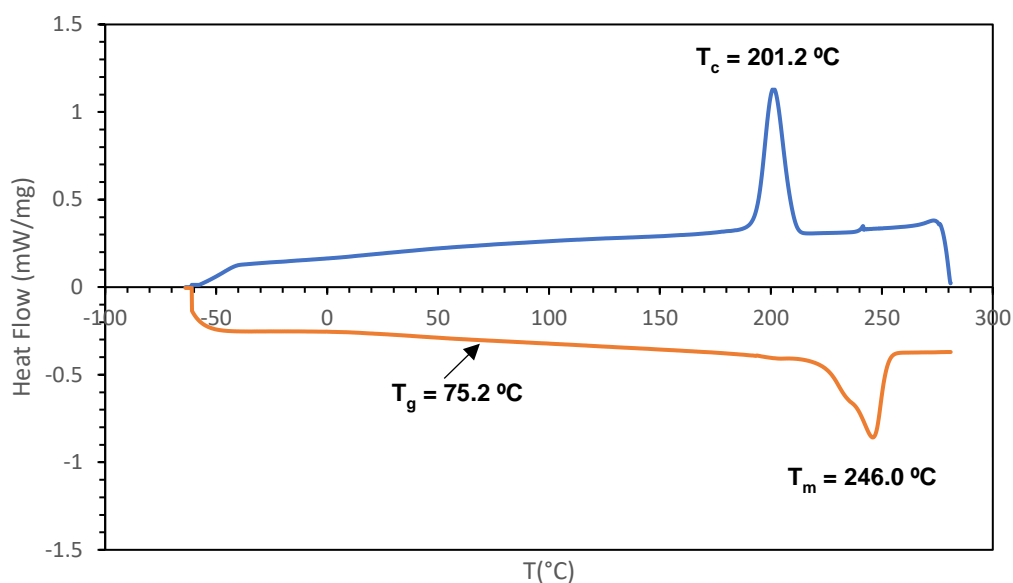


Fig. S9 Thermal transitions in precipitated PET sample using 40(v/v)% water and ethanol mixture. Blue line denotes cooling cycle, while green line denotes the heating cycle.

Powder X-ray Diffraction

The powder X-ray diffraction (PXRD) data were collected in a D8 Advance Bruker AXS q-2q diffractometer, with a generator operating on the voltage of 40kV and a current of 30mA equipped with a LYNXEYE detector. A point beam of a copper radiation source ($\text{Cu K}\alpha$, $\lambda = 1.5406\text{ \AA}$) was employed for the experiments. The samples were scanned at a diffraction angle 2θ in the range of 5° to 80° with 0.05° step and 441.6s per step at room temperature 25°C .

Viscosity Measurements

Viscosity Measurements were carried out at 298.15 K and atmospheric pressure using a using an SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter, where the standard uncertainty for the temperature is 0.02 K. The repeatability of dynamic viscosity of this equipment is 0.35%, respectively. Triplicates of each sample were performed to ensure accuracy and the reported results are the average values. Moreover, the relative standard uncertainty in viscosity was calculated by the ratio of the standard deviation and the average of the three replicates of each sample, where the highest absolute standard uncertainty registered for the dynamic viscosity measurements was 0.04 mPa.s. Solutions of pristine PET and recycled PET were prepared using 1,1,1,3,3,3-Hexafluoro-2-propanol supplied by Sigma Aldrich with purity of 99+%.

The values obtained of the intrinsic viscosity, $[\eta]$, for both the virgin and the precipitated PET were calculated as the intercept of the equation (E3).

$$\frac{\eta_{SPC}}{C} = a + b C \quad (E3)$$

where, η_{SPC} denotes the specific viscosity, C the polymer concentration in the specific solvent and a and b are the fitting coefficients.

The coefficients of the linear fits of equation E3 to the data obtained from pristine PET and the precipitated PET both in 1,1,1,3,3,3-Hexafluoro-2-propanol are listed in Table S3 and represented in Fig. S10.

Table S3 Coefficients of the linear fits of equation E2 to the data obtained from pristine PET and the precipitated PET in 1,1,1,3,3,3-Hexafluoro-2-propanol and respective correlation coefficient. The value of the intrinsic viscosity for both cases is also listed.

PET	a	b	R ²	$[\eta]$ /(dl/g)
Pristine	0.0037 ± 0.0003	0.078 ± 0.004	0.9561	0.78 ± 0.04
Precipitated	0.0015 ± 0.0002	0.063 ± 0.002	0.9659	0.63 ± 0.02

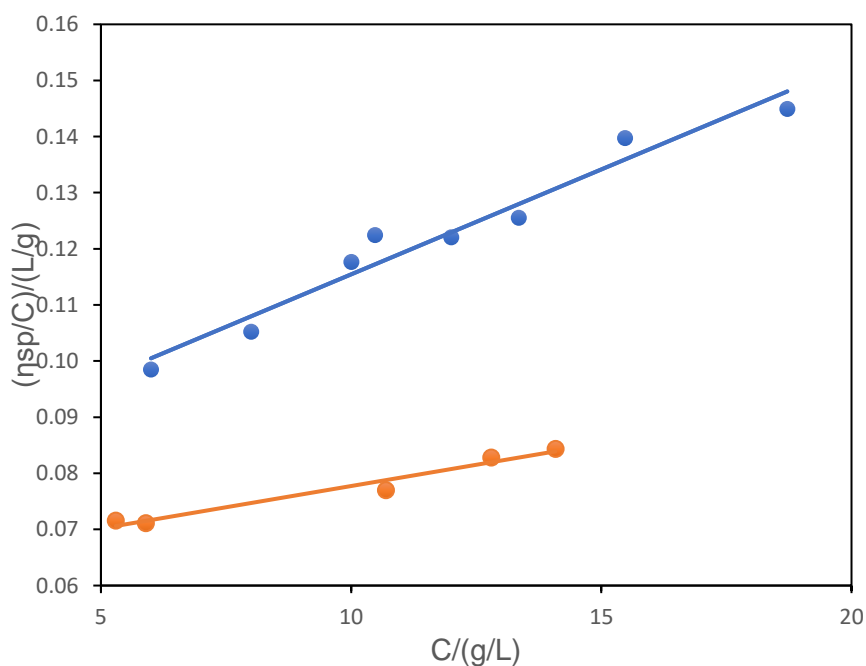


Fig. S10 Specific viscosity of PET solution divided by the concentration of PET in solution (η_{sp}/C) versus Concentration of PET in solution (g/L) at 20°C. Green series represents the pristine PET, while blue series represents the precipitated PET.

PET Recycling

Fig. S11, S12 and S13 show the ^1H NMR spectra of thymol:carvacrol (1:1) fresh, after the 1st and the 2nd cycle respectively. After the first cycle, the addition of 40(v/v)% mixture of water and ethanol, in the 1:5 (w/v) DES to mixture proportion, leads to the formation of two phases. ^1H NMR of the DES phase is presented in Fig. S12. The same does not happen after the second cycle, where the addition of the mixture leads to one phase, probably due to presence of water from the first cycle. ^1H NMR of the one phase containing DES, ethanol and water is presented in Fig. S12. However, the addition of DES leads to phase separation and the recovery of solubilized DES.

Generally, these spectra show the chemical stability of thymol:carvacrol (1:1) throughout the 2 recycling cycles¹. In Fig. S12, after the 1st recycling cycle, a new peak is found at $\delta = 4.5$ ppm in comparison with Fig. S11, marked as a) in the spectra. This peak is probably due to CH_2 groups adjacent to $-\text{COO}$ groups in small molecular weight PET molecules², in agreement to what was observed in the viscosity experiments, where a small decrease in PET molecular weight was observed. NMR spectra were recorded on AMX-400 and Avance II 500 MHz spectrometers (Bruker) at 25 °C

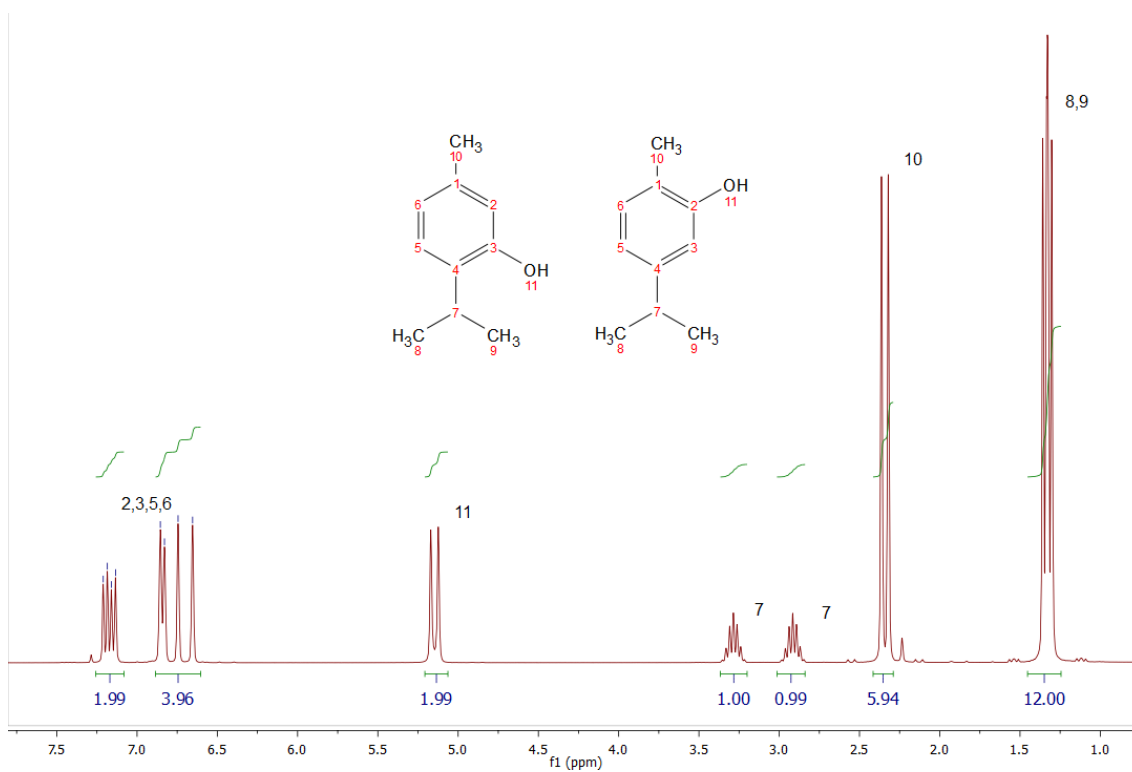


Fig. S11. ^1H NMR of thymol:carvacrol (1:1) in deuterated chloroform.

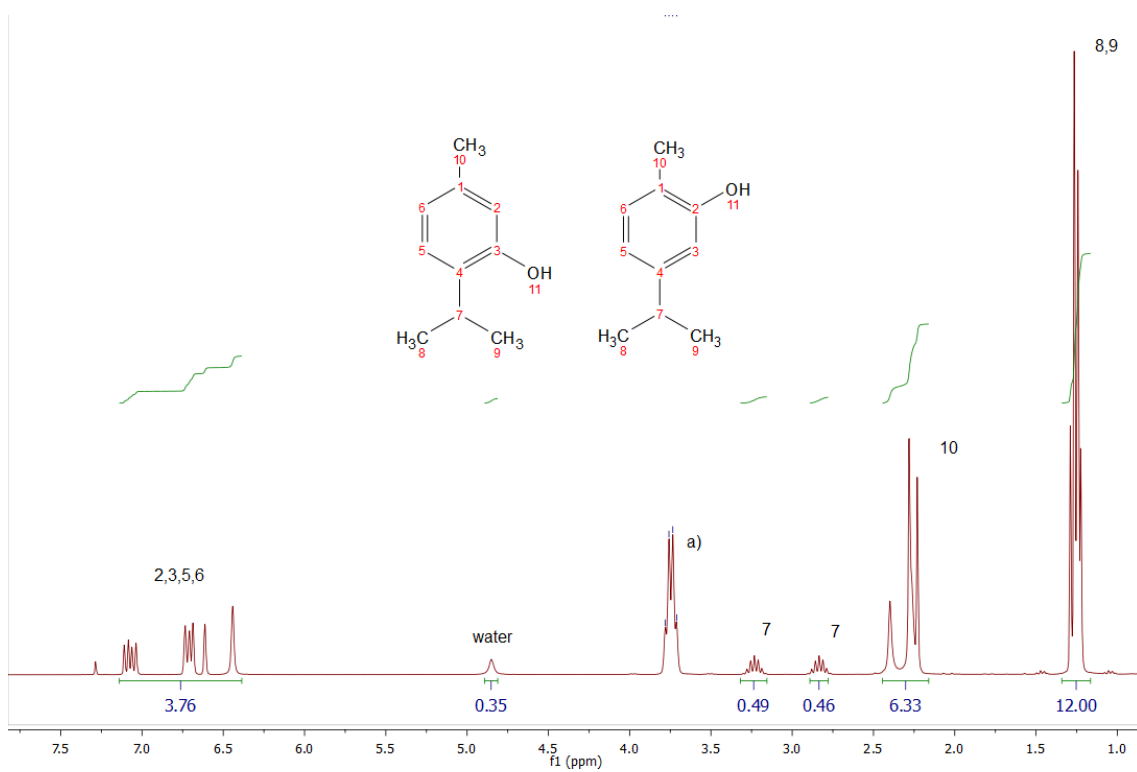


Fig. S12. ¹H NMR of thymol:carvacrol (1:1) after the 1st cycle in deuterated chloroform.

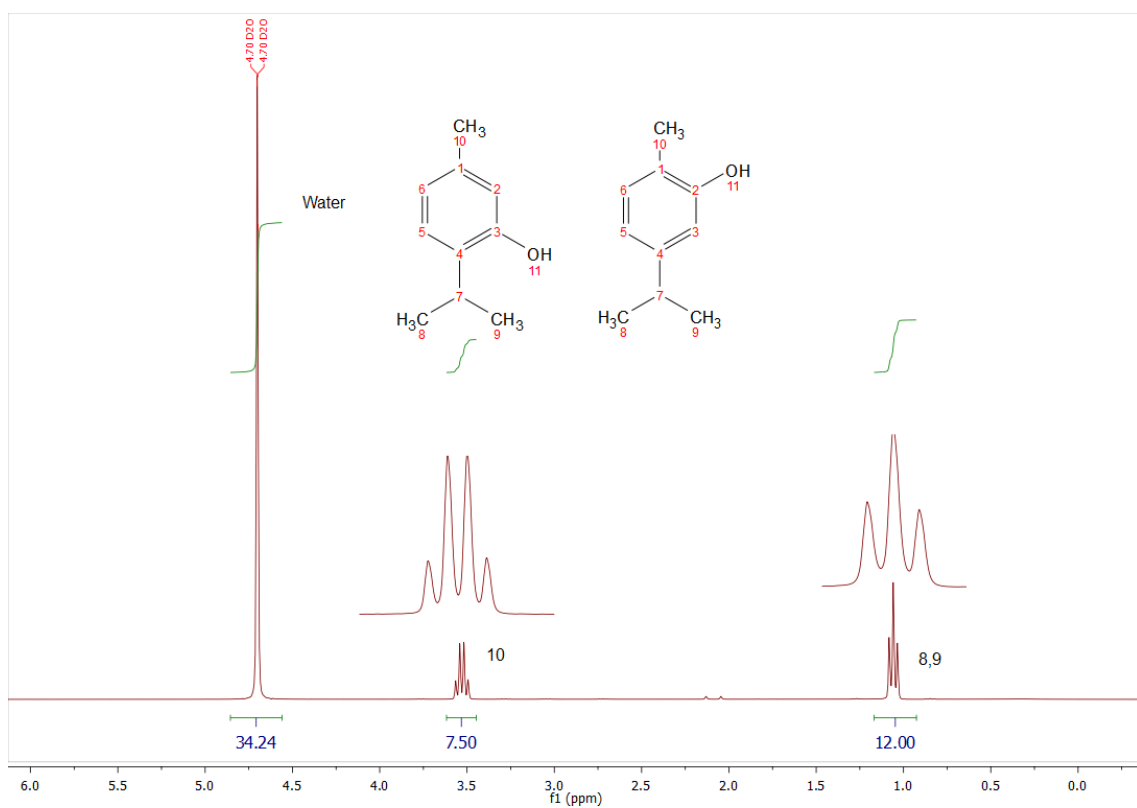


Fig. S13. ¹H NMR of thymol:carvacrol (1:1) after the 2nd cycle in deuterated water.

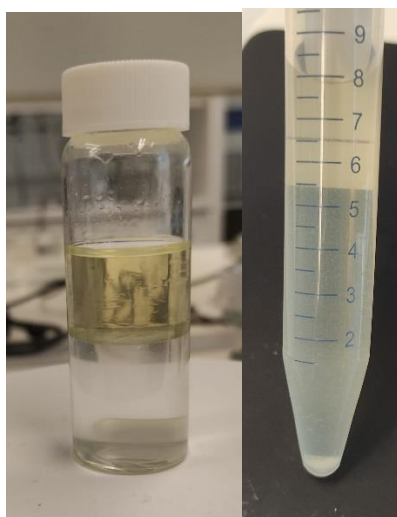


Fig. S14. Liquid phase after the 1st cycle (left) and the 2nd cycle (right).

Fig. S15 compares precipitated of PET after the 1st cycle (yellow)) and precipitated PET after 2nd cycle (orange). This FTIR was acquired using a Jasco 430. Each FTIR spectrum presented was based on a recording of 16 scans at a resolution of 4 cm⁻¹. As it can be seen, identical fingerprints for both polymers can be observed.

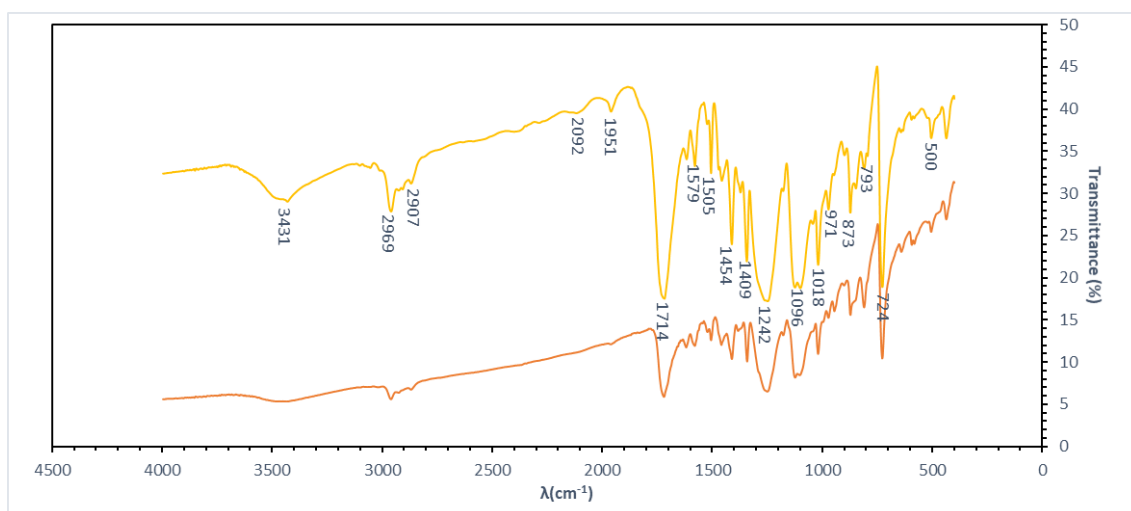


Fig. S15. FTIR spectra precipitated of PET after the 1st cycle (yellow)) and precipitated PET after 2nd cycle (orange).

In what concerns the PET precipitation, a yield of 100% was obtained for each one of the recycling cycles. As for the recovery of DES, a full recovery was also achieved. However, vigorous stirring, vortexing and shaking was needed to guarantee that no DES stays inside the PET structure. It is also very important to dry the DES after each cycle so that no water is carried out to the next cycle, hindering PET precipitation and two liquid phases formation.

1. A. L. Carbone-Howell, N. D. Stebbins, and K. E. Uhrich, *Biomacromolecules*, 2014, **15**, 1889–1895.
2. Z. Han, Y. Wang, J. Wang, S. Wang, H. Zhuang, J. Liu, L. Huang, Y. Wang, W. Wang, L. A. Belfiore, J. Tang, *Materials*, 2018, **11**, 587.