

Supporting Information

Chemical Recycling of Post-Consumer PET into High-Performance Polymer Aerogel

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1. Materials

All the chemicals including vanillin, ethylene carbonate, Na_2CO_3 , DMSO, DMSO- d_6 , CDCl_3 , dibutyltin oxide (DBTO), Diethylenetriamine (DETA), p-Phenylenediamine (PDA), 4,4'-Methylenedianiline (MDA) and tris(2-aminoethyl) amine (TREN) are commercially available and could be used without further purification if not mentioned. PET particles and PET powder are obtained by crushing PET bottle scraps ($M_n=20799$ g/mol, $M_w=44834$ g/mol, measured by GPC with hexafluoroisopropanol as mobile phase). PET and cotton fabrics are purchased commercially and used after washing with isopropanol.

2. Characterization methods

NMR: ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX-300, ARX-400 and ARX-500 spectrometer at ambient temperature in deuterated chloroform (CDCl_3), Deuterated water (D_2O) or dimethylsulfoxide (DMSO) with tetramethylsilane (TMS) as the internal reference. Chemical shifts were reported in ppm from the internal standard, tetramethylsilane (0 ppm) for ^1H NMR, solvent proton shifts (ppm): CDCl_3 , 7.26 (s); D_2O , 4.79 (s); DMSO- d_6 , 2.50 (s).

IR: FT-IR spectra of the samples were recorded on a VERTEX-70 IR spectrometer (Bruker) with a scanning range from 4000 to 500 cm^{-1} . ATR spectra of the samples were recorded on an INVENIO-R IR spectrometer (Bruker) with a scanning range from 4000 to 500 cm^{-1} .

ESI-MS: Electro spray ionization Mass spectroscopy was conducted on a system composed of a Waters Quattro, Premier XE. The system was operated with Full Scan

function type, 3.0 kV Capillary, 20 V Cone, 110 °C Source Temperature, 80 L/Hr Cone Gas Flow, 380 °C desolvation temperature and 600 L/Hr Desolvation Gas Flow.

TGA: Thermo gravimetric analyses were measured on a Perkin-Elmer DSC-7 instrument under N₂ atmosphere with a heating rate of 10 °C min⁻¹ from 25 °C temperature to 800 °C

DSC: Differential scanning calorimetry analysis was performed on a Perkin-Elmer DSC-7 instrument under N₂ atmosphere. The sample was first heated from -50 °C to 200 °C at 10 °C min⁻¹ and then rapidly quenched to -50 °C, followed by a second heating process to obtain the glass transition temperature (T_g).

Skeletal density: The skeletal density was measured using an ULTRAPYC 1200e automatic density analyzer. The system was configured to operate at an analysis temperature of 25 °C, with nitrogen (N₂) as the gas type. The target pressure was set at 10.0 psig, with a flow purge duration of 5.0 minutes, and a maximum of 5 runs were conducted.

BET: The specific surface area and pore size distribution of the aerogels were analyzed by Brunauer–Emmett–Teller (BET) analyzer (Quantachrome). Before measurement, RPA-3,4 was outgassed at 50 °C for 10 h under vacuum condition, RPA-1,2 was outgassed at 100°C for 10 h under vacuum condition.

Cyclic compression test: Cyclic compression test was conducted by electronic universal testing machine with the compression rate of 5 mm/min. Aerogels with sample dimensions of 24 mm diameter and 12 mm thickness were used.

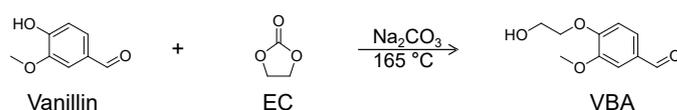
Thermal diffusivities: The thermal diffusivities (α) of the composites were measured by the laser flash method using LFA 467 (Nano-flash, Netzsch) at room temperature. The method is compliant with the international standards ASTM E1461-13. Data were averaged over at least three measurements.

SEM: The field emission scanning electron microscopy was collected through the Zeiss lens in Merlin (1.0~2.0 nm (1 KV); Acceleration voltage: 0.02~30 KV; Beam strength: 1 pA-100 Na; Detector: Everhart-Thornley secondary electron detector of the photocoupled photomultiplier tube). The aerogel samples were sputtered with gold for 40 s before testing.

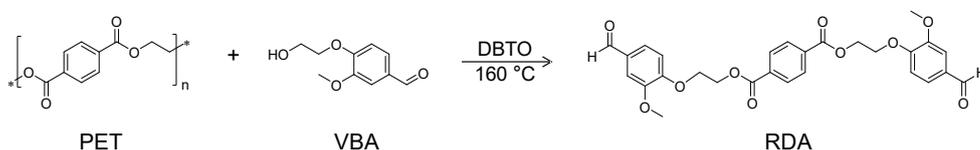
3. Experimental Procedures and Discussion

3.1 General synthesis procedure

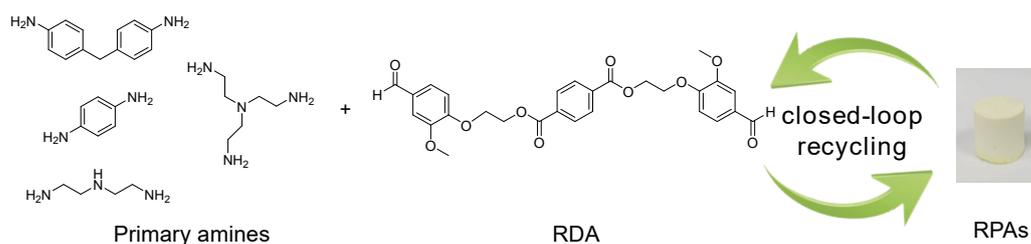
(a) Synthesis of vanillin-based alcoholysis agent



(b) Alcoholysis of PET using VBA



(c) Synthesis and hydrolysis recycling of RPAs



Scheme S1. Synthetic scheme of the upcycling routes from PET to RPAs.

Synthesis of VBA: Vanillin (120 g, 0.79 mol), ethylene carbonate (70.84 g, 0.80 mol) and Na_2CO_3 (1.68 g, 0.016 mol) were added in a 1000 ml flask and reacted at $165\text{ }^{\circ}\text{C}$ for 3 h with magnetic stirring and nitrogen protection. The crude product was dissolved by chloroform and washed with water until the aqueous phase becomes colorless. Subsequently, the organic phase underwent complete desiccation, and the crude product was recrystallized through chloroform and n-hexane, resulting in the acquisition of a white powdered substance with a yield of 78.1%.¹

Synthesis of RDA: Typically, PET (0.98 g, 5.1 mmol repeating units) powder, VBA (4.0 g, 20.4 mmol), and DBTO (0.03 g, 0.12 mmol) were combined in a 20 ml reaction tube, which was then heated to $160\text{ }^{\circ}\text{C}$ and maintained at this temperature for 24 h. The resultant reaction mixture was thoroughly rinsed with 20ml of ethyl acetate, after which the solid phase crude product was isolated by filtration and collected. This product underwent recrystallization using chloroform and n-hexane, yielding a white powder product with a 61% recovery rate. In the alcoholysis reaction of PET fibers, commercially purchased PET fabric was served as the PET source, and 0.49 g of cotton cloth was utilized in the blended group.

Synthesis of RPA-1: A 0.1 g/ml TREN solution was prepared by dissolving TREN in DMSO. To a 20 ml glass vial, 1.0 g of RDA (1.91 mmol) and 0.1903 g of MDA (0.96 mmol) were added along with 11.9 ml of DMSO. The mixture was heated in an oil bath at $120\text{ }^{\circ}\text{C}$ until RDA and MDA were completely dissolved, followed by magnetic stirring for 1 hour at the same temperature. Then, 0.94 ml of the TREN solution (0.64 mmol) was added, and the mixture was stirred magnetically for another hour at $120\text{ }^{\circ}\text{C}$.

The vial was then left at room temperature to cool gradually, during which gelation occurred. After reaching room temperature, the gel was left to age for 12 hours. To counteract the volumetric shrinkage from DMSO crystallization, approximately 5 ml of DMSO was then introduced into the vial. The vial was subsequently placed in a freezer at -18 °C to ensure complete crystallization of the DMSO. Finally, the DMSO was removed by freeze-drying, resulting in the formation of RPA-1.

Synthesis of RPA-2: A 0.1 g/ml TREN solution was prepared by dissolving TREN in DMSO. To a 20 ml glass vial, 1.0 g of RDA (1.91 mmol) and 0.1038 g of PDA (0.96 mmol) were added along with 11.0 ml of DMSO. The mixture was heated in an oil bath at 120 °C until RDA and PDA were completely dissolved. It was then stirred magnetically for 1 hour at the same temperature. Following this, 0.94 ml of the TREN solution (0.64 mmol) was added to the mixture, which was stirred magnetically for an additional hour at 120 °C. The vial was then left at room temperature to cool gradually, during which gelation occurred. After reaching room temperature, the gel was left to age for 12 hours. To accommodate the volumetric shrinkage due to DMSO crystallization, approximately 5 ml of DMSO was added to the vial. The vial was then placed in a freezer at -18 °C to ensure full crystallization of DMSO. Finally, the DMSO was removed by freeze-drying, leading to the formation of RPA-2.

Synthesis of RPA-3: A 0.1 g/ml TREN solution was prepared by dissolving TREN in DMSO. Into a 20 ml glass vial, 1.0 g of RDA (1.91 mmol) and 0.0990 g of DETA (0.96 mmol) were combined with 11.0 ml of DMSO. The mixture was heated in an oil bath at 120 °C until RDA and DETA were completely dissolved, followed by magnetic stirring for 1 hour at the same temperature. Then, 0.94 ml of the TREN solution (0.64 mmol) was added, and the mixing was continued with magnetic stirring for an additional hour at 120 °C. The vial was set aside at room temperature to cool, during which gelation occurred. After reaching room temperature, the gel was left to age for 12 hours. To account for the volume reduction due to DMSO crystallization, about 5 ml of DMSO was added to the vial. The vial was then placed in a freezer at -18 °C to ensure full crystallization of DMSO. Finally, the DMSO was removed by freeze-drying, leading to the formation of RPA-3.

Synthesis of RPA-4: TREN was dissolved in DMSO to prepare 0.1 g/ml TREN solution. A total of 1.0 g (equivalent to 1.91 mmol) of RDA was introduced into a 20 ml glass bottle, along with 10 ml of DMSO. Following the complete dissolution of the RDA through heating in an oil bath at a temperature of 120 °C, 1.31 ml TREN solution (equivalent to 0.896 mmol) was introduced into the mixture. The resulting solution was subjected to magnetic stirring for a duration of 1 hour at a temperature of 120 °C. Subsequently, 0.56 ml of TREN solution (equivalent to 0.384 mmol) was introduced into the solution, resulting in an immediate observation of gelation. Following the gelation, the reaction proceeded at a temperature of 120 °C for a duration of 5 minutes. Next, put the glass bottle at ambient temperature in order to facilitate gradual cooling. Following the attainment of ambient temperature, the gel was subjected to a 12-hour

period of aging under room temperature conditions. Subsequently, approximately 5 ml of DMSO was added into the glass bottle in order to mitigate the impact of volume shrinkage on the gel as a result of DMSO crystallization. Following that, the glass bottle was placed in the refrigerator at -18 °C to fully crystallize DMSO. Subsequently, the DMSO was thoroughly eliminated through freeze drying, resulting in the formation of RPA-4.

Acid hydrolysis recycling of RPA-4: RPA-4 (0.92 g) was added into 50 ml 0.1 M HCl/THF solvent. The reaction system was stirred at ambient temperature for a duration of 12 hours. During this process, RPA-4 underwent complete hydrolysis, resulting in the formation of light yellow solid powder and a light yellow solution. The resultant product was subsequently filtered and washed twice with deionized water. The light yellow powder product in solid phase was gathered and dried to yield 0.74 g of RDA (96% recycling rate). The filtrate was combined and thereafter subjected to concentration using rotary evaporation. After that, OH⁻ ion exchange resin was added into the solution until the pH surpasses a value of 10. The mixture was reacted at ambient temperature for a duration of 6 hours, after which the ion exchange resin can be separated from the solution by filtration. Upon complete drying of the filtrate, 0.13 g TREN is obtained with a recycling rate of 90%.¹⁻⁴

Acid hydrolysis recycling of RPA-4 from mixed waste stream: A mixture of plastic waste include RPA-4 (0.92 g), PP, PET and HDPE was added into 50 ml 0.1 M HCl/THF solvent. The reaction system was stirred at ambient temperature for a duration of 12 hours. During this process, RPA-4 underwent complete hydrolysis, resulting in the formation of light yellow solid powder and a light yellow solution, while the residual plastic waste remained unreactive. The resultant product was subsequently filtered and washed twice with deionized water. The light yellow powder product in solid phase was gathered and dried to yield 0.74 g of RDA (96% recycling rate). The filtrate was combined and thereafter subjected to concentration using rotary evaporation. After that, OH⁻ ion exchange resin was added into the solution until the pH surpasses a value of 10. The mixture was reacted at ambient temperature for a duration of 6 hours, after which the ion exchange resin can be separated from the solution by filtration. Upon complete drying of the filtrate, 0.13 g TREN is obtained with a recycling rate of 90%.¹⁻⁴

3.2 Synthesis of vanillin-based alcoholysis agent

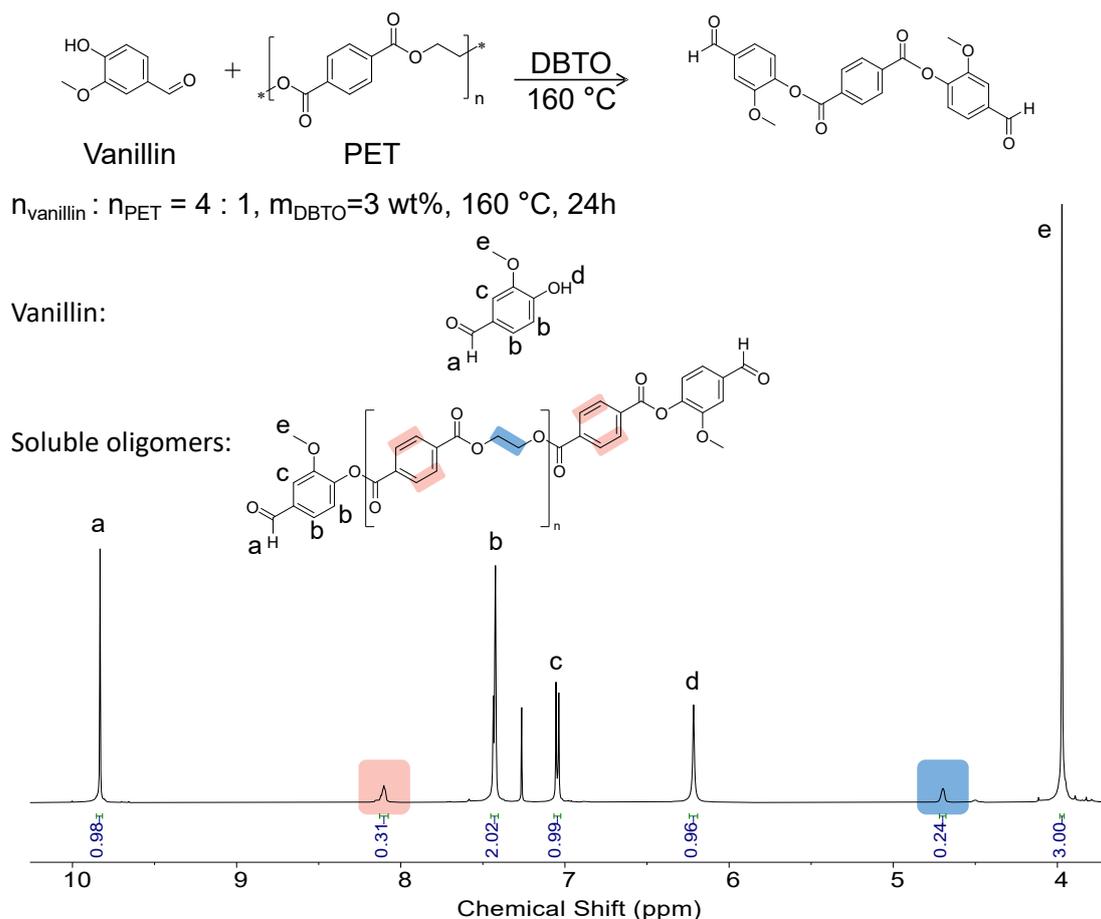


Figure S1. Depolymerization of PET through vanillin, $^1\text{H-NMR}$ result showed that only a small amount of PET transformed into soluble oligomers after 24 hours of reaction.

$$\text{Conv.}_{\text{PET}} = \frac{n_{\text{reacted PET}}}{n_{\text{PET}}} = \frac{n_{\text{reacted PET}}}{\frac{1}{4}n_{\text{vanillin}}} = \frac{\delta(8.10) \div 4}{\frac{1}{4}\delta(7.03)} \times 100\% = 31\%$$

Alcoholysis of PET using vanillin: Vanillin (3.17 g, 20.8 mmol), PET (1.00 g, 5.2 mmol repeating units, 0.15 mm particle size) and DBTO (0.03 g, 0.12mmol) were added in a 20 ml reaction tube and reacted with magnetic stirring at $160\text{ }^\circ\text{C}$ for 24 h. The hydrogen signals of the benzene ring area (8.1 ppm) and the methyl group area (4.7 ppm) in $^1\text{H-NMR}$ result indicate that PET was partially depolymerized into soluble oligomers (Fig. S1). However, this low conversion rate and incomplete depolymerization suggest that vanillin is not suitable for PET alcoholysis.

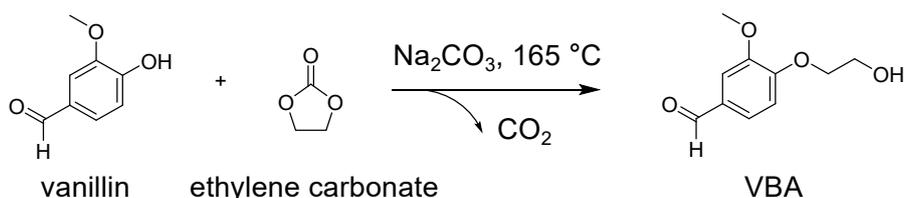


Figure S2. Synthesis of VBA through the interaction between vanillin and ethylene carbonate

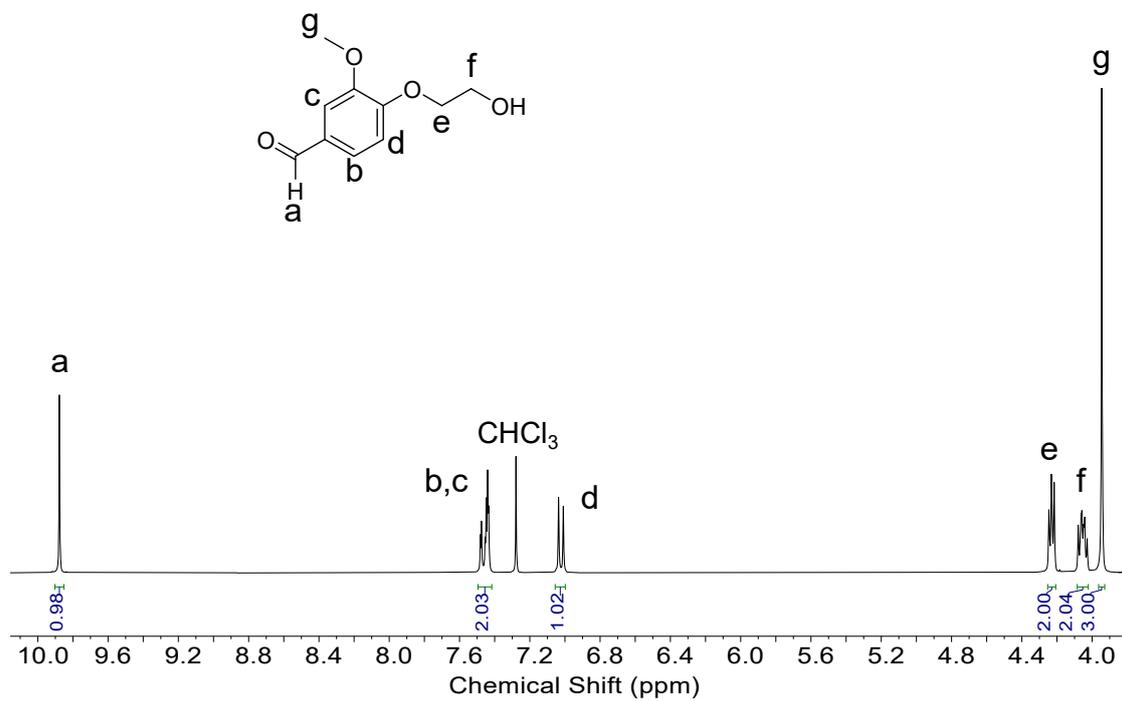


Figure S3. ¹H NMR spectrum of VBA (CDCl₃ at 25 °C, 500 MHz).

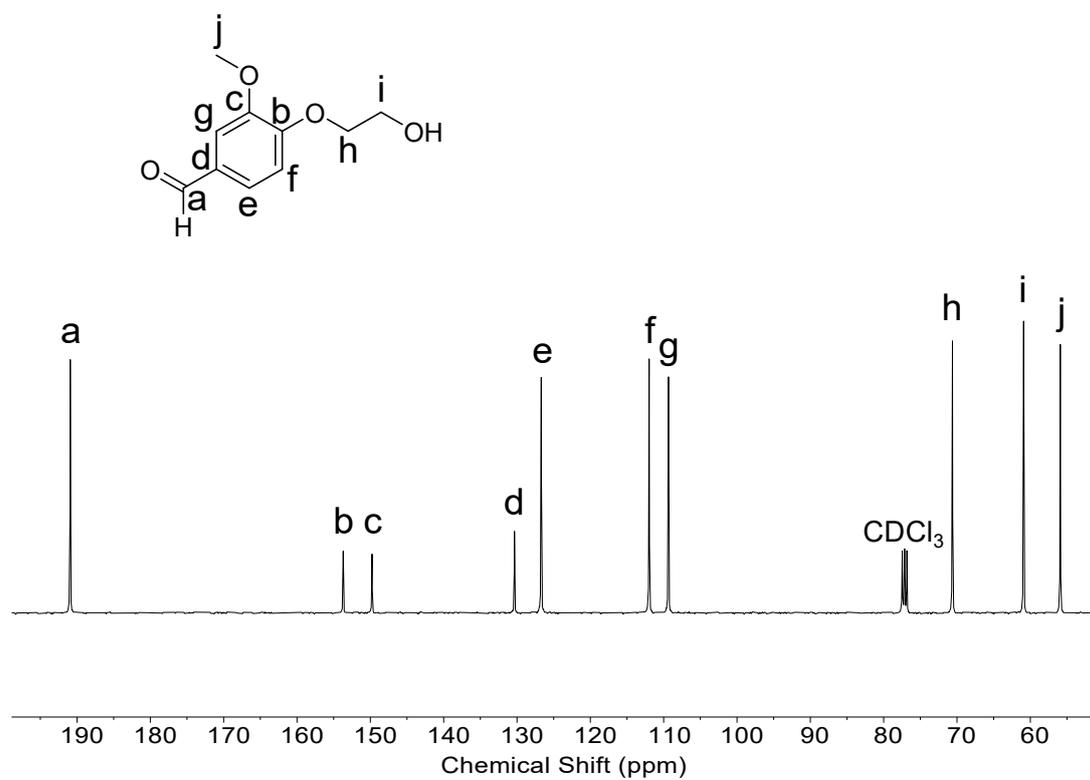


Figure S4. ¹³C NMR spectrum of VBA (CDCl₃ at 25 °C, 400 MHz).

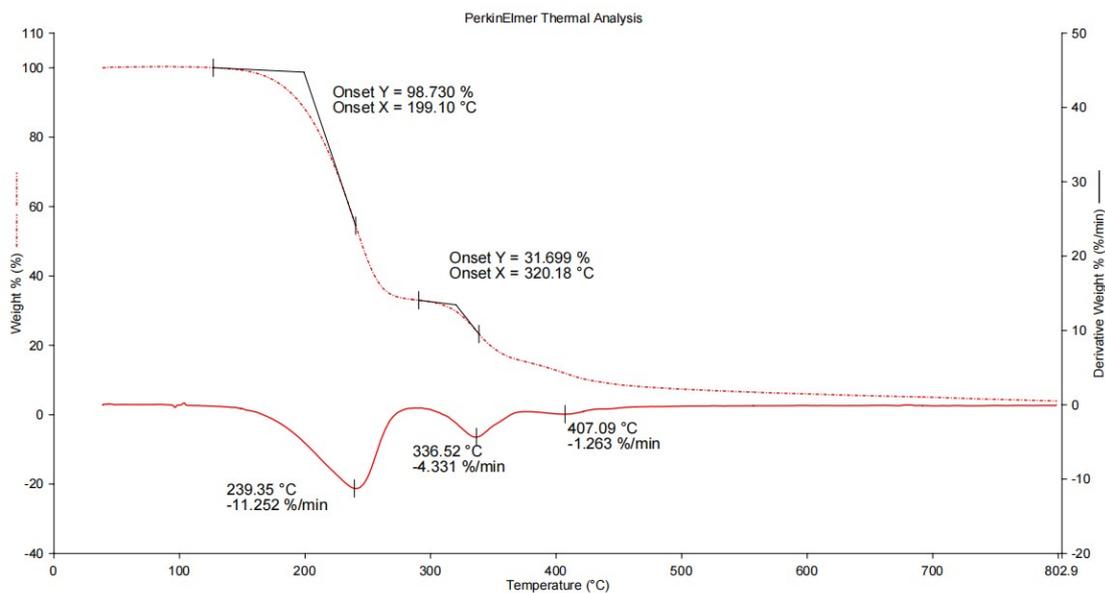


Figure S5. TGA and DTG results of VBA. (Atmosphere: N₂, rate: 10 °C/min)

3.3 Synthesis and characterization of r-PET dialdehyde

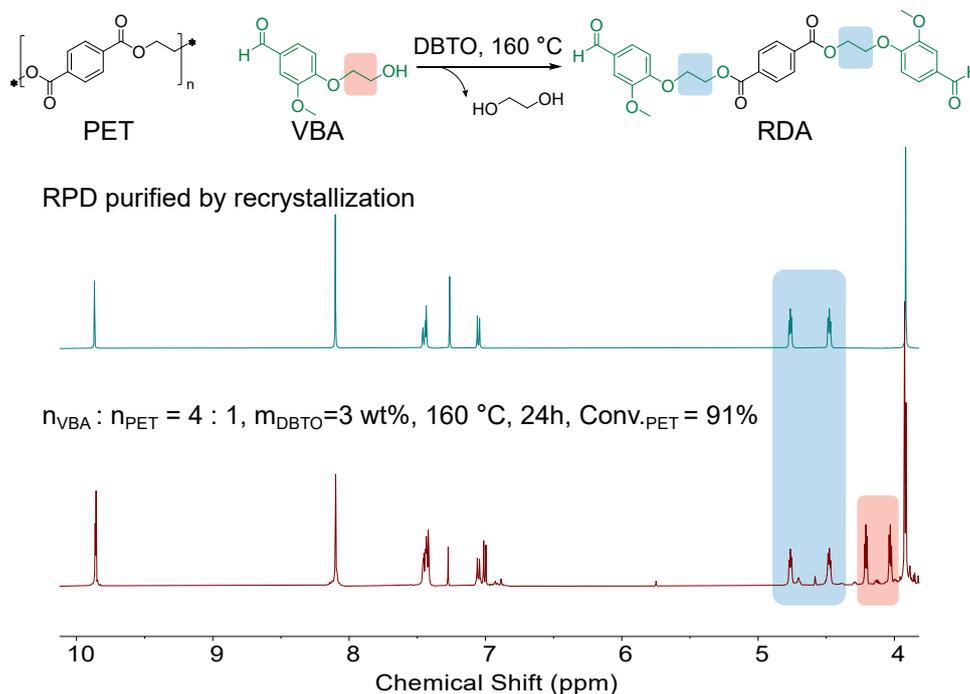


Figure S6. ¹H NMR spectrum of the reaction liquid and purified RDA (CDCl₃ at 25 °C, 500 MHz). The conversion of PET was calculated by the characteristic peak of methylene at 4-5 ppm.

$$Conv_{PET} = \frac{n_{RDA}}{n_{PET}} = \frac{n_{RDA}}{\frac{1}{4}n_{VBA}} = \frac{[\delta(4.49) + \delta(4.78)] \div 8}{\frac{1}{4}[\delta(4.49) + \delta(4.78) + \delta(4.05) + \delta(4.20)] \div 4} \times 100\% = 91\%$$

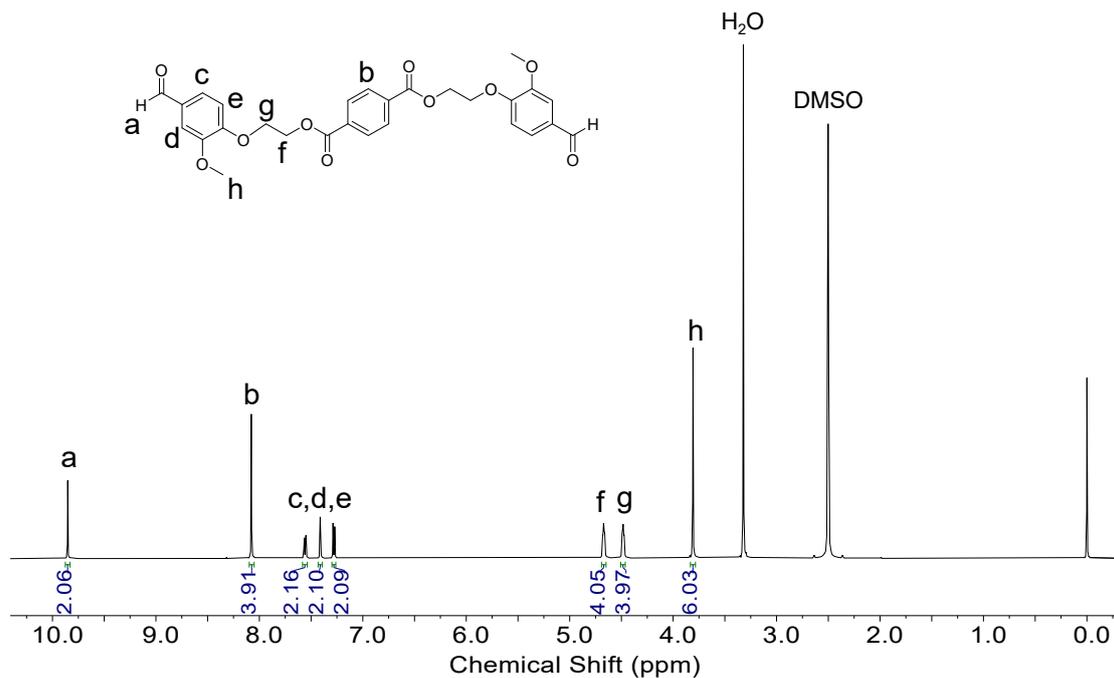


Figure S7. ¹H NMR spectrum of RDA (DMSO-d₆ at 25 °C, 500 MHz).

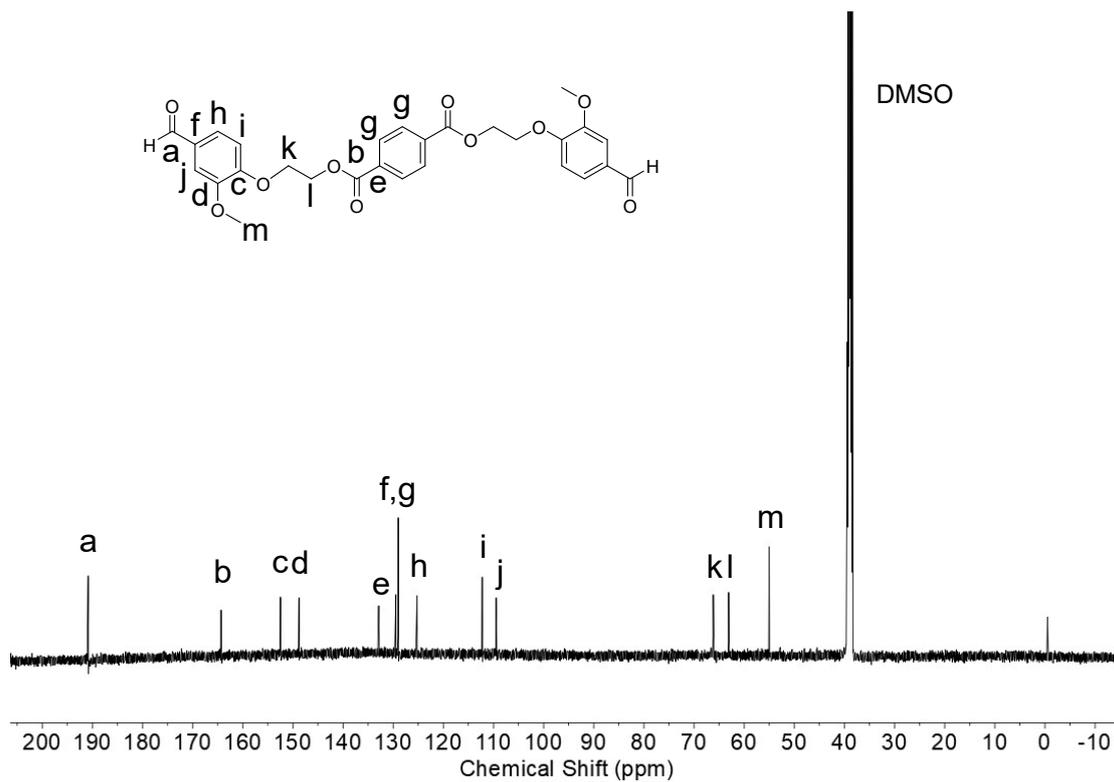


Figure S8. ¹³C NMR spectrum of RDA (DMSO-d₆ at 25 °C, 500 MHz).

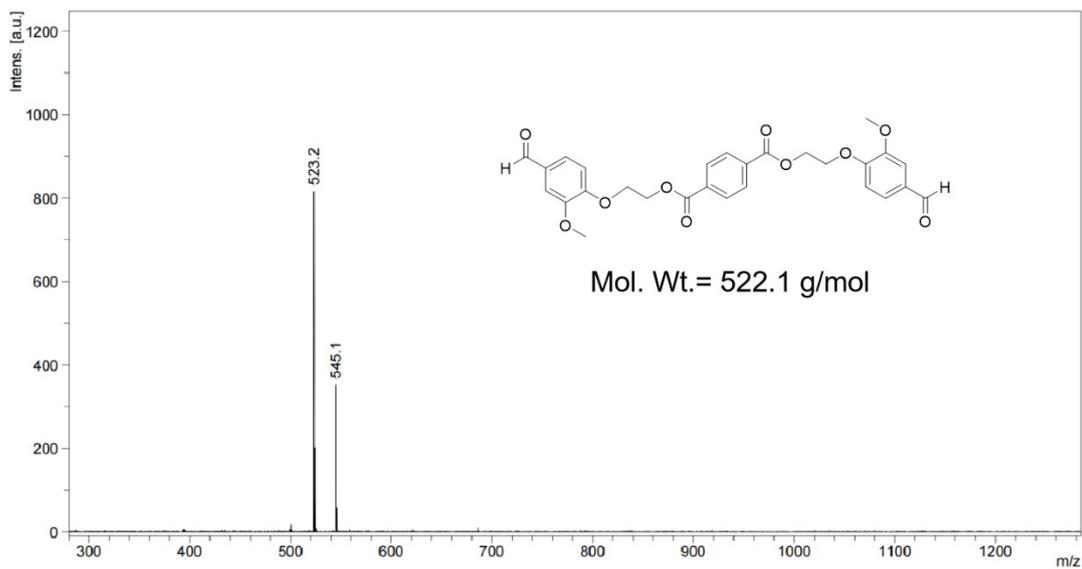


Figure S9. ESI-MS of RDA. Peaks at 523.2 and 545.1 are assigned to RDA+H⁺ and RDA+Na⁺, respectively.

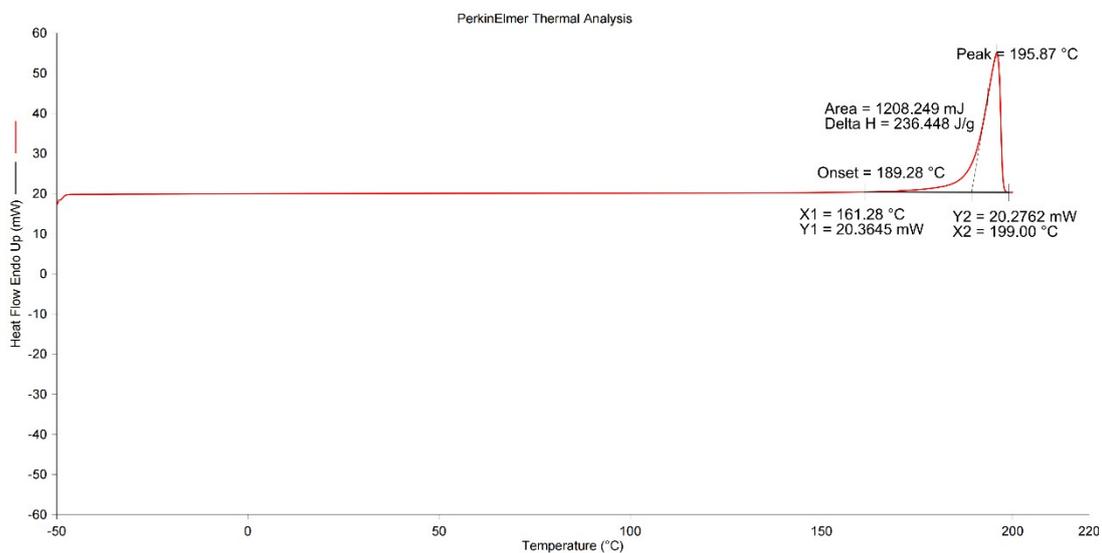


Figure S10. DSC result of RDA. $T_m = 195.87$ °C.

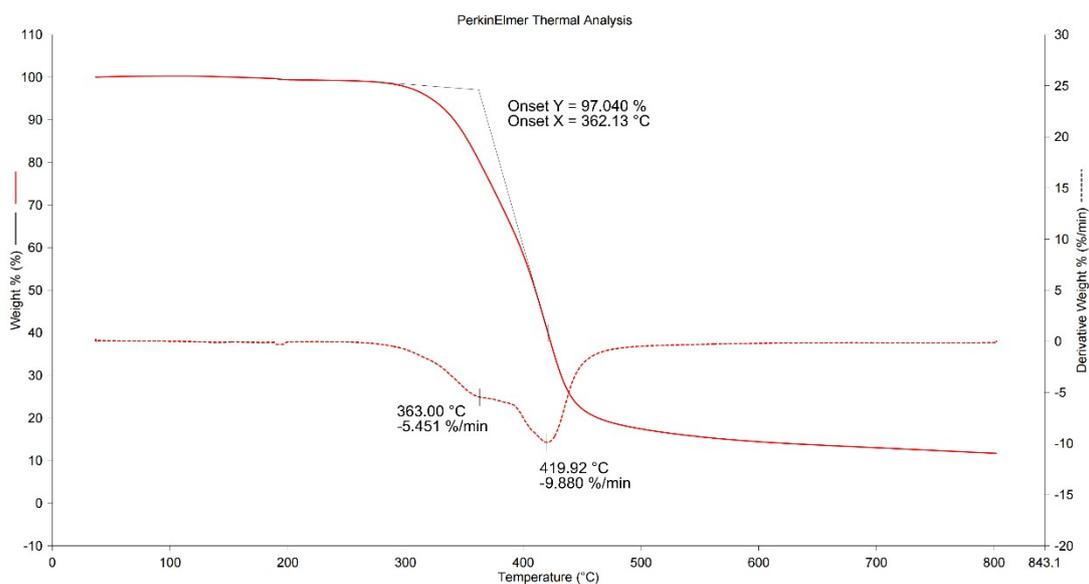


Figure S11. TGA and DTG results of RDA. ($T_{d,5\%} = 321.6$ °C, Atmosphere: N_2 , rate: 10 °C/min)

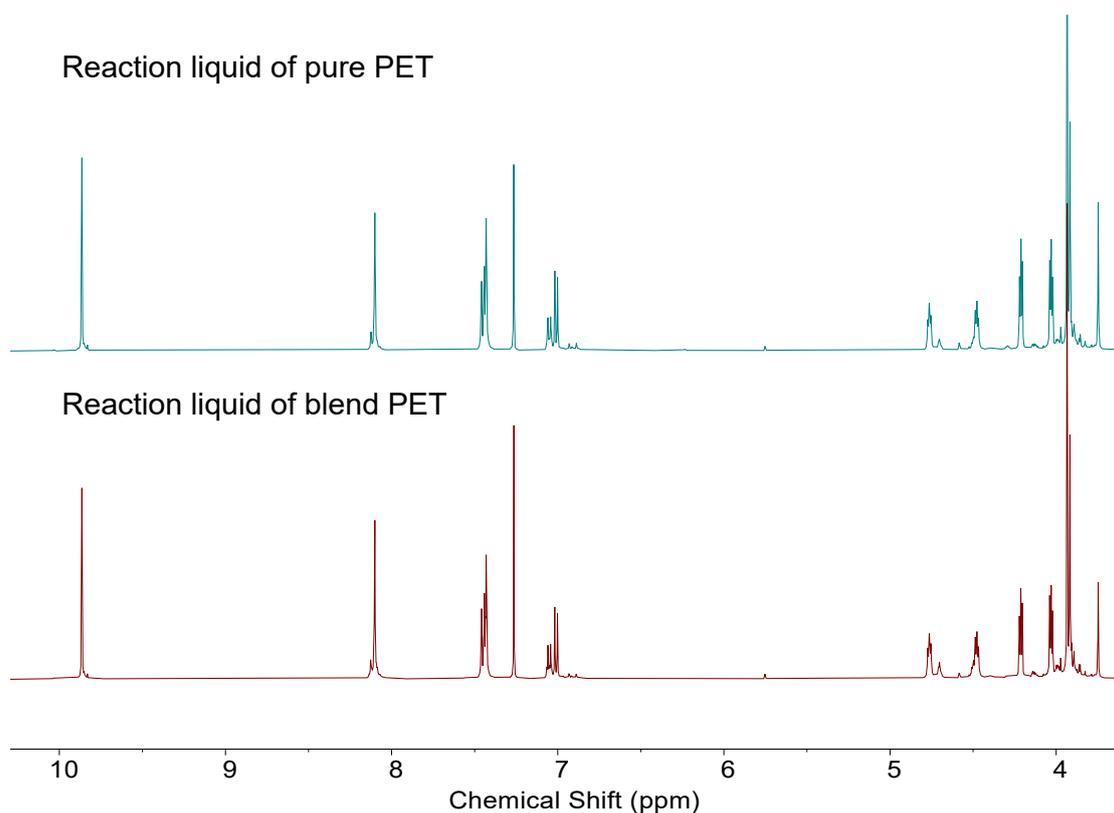


Figure S12. 1H -NMR spectrum of the blend PET and pure PET reaction liquid ($CDCl_3$ at 25 °C, 500 MHz). The consistency indicates the chemical inertia of cotton fibers during reaction.

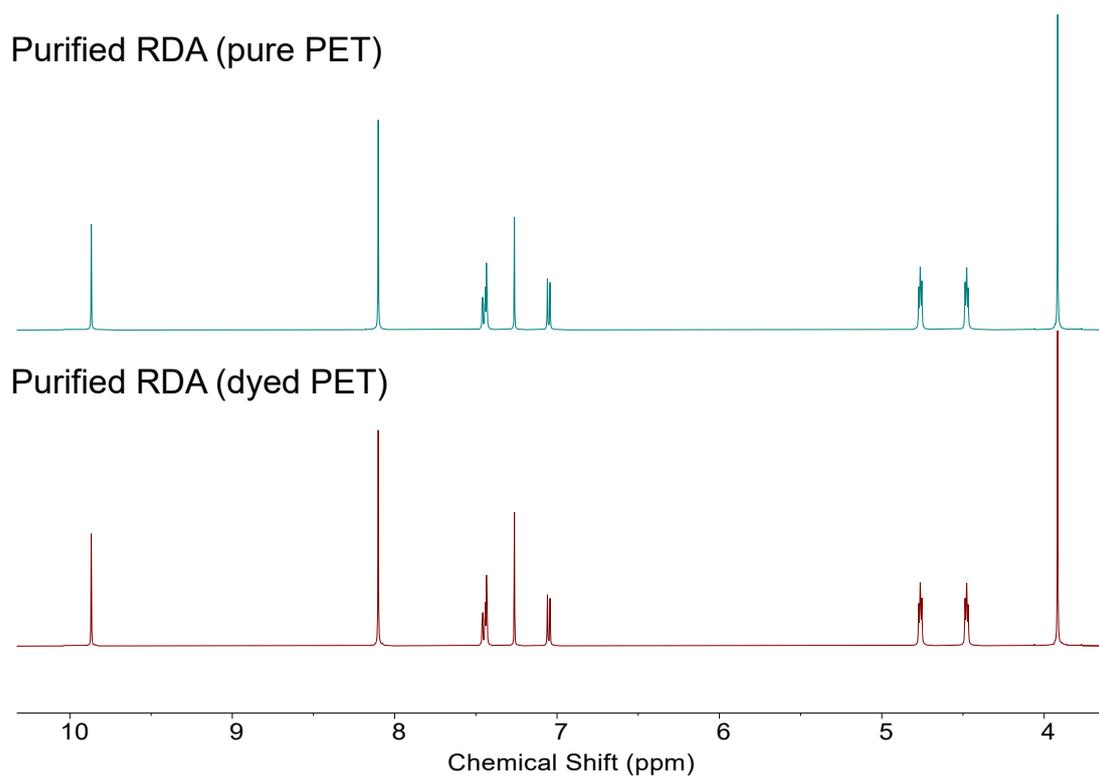


Figure S13. ^1H -NMR spectrum of RDA recycling from pure and dyed PET (CDCl_3 at 25°C , 500 MHz). The ^1H NMR results indicate that using dyed PET as the PET source can yield RDA products consistent with pure PET.



Figure S14. Images of PET fibers, dyed PET fibers, PET powder (0.15 mm particle size) and PET particles (5 mm particle size).

3.4 Synthesis and characterization r-PET aerogel

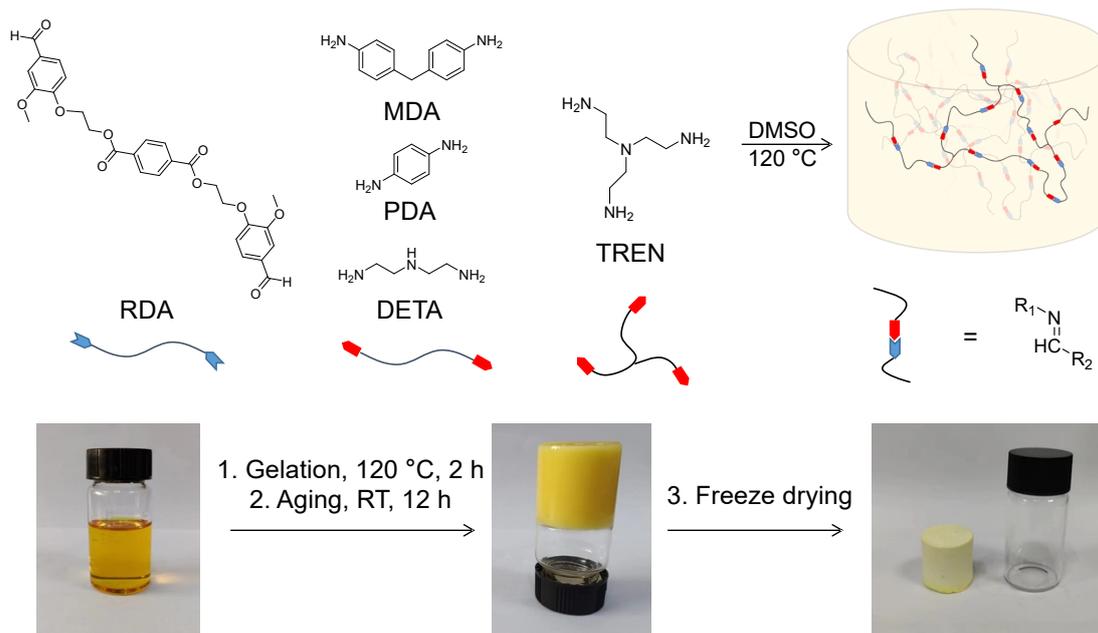


Figure S15. Images illustrating the synthesis of RPAs.

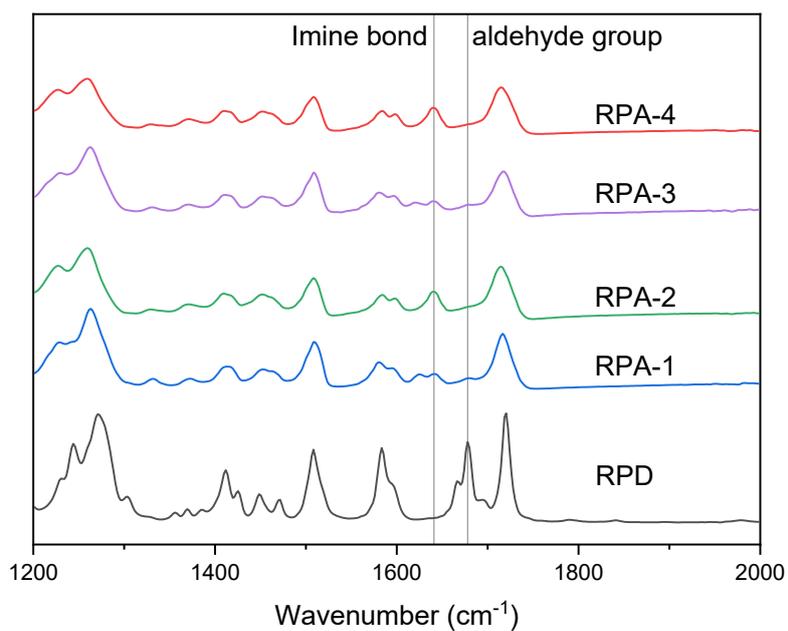


Figure S16. ATR FT-IR results of RDA and RPA-1~4. The absorption peak at 1678 cm⁻¹ corresponds to the aldehyde group in RDA. The absorption peak at 1641 cm⁻¹ corresponds to the imine bond in RPAs.

Table S 1 Formula and basic properties of RPAs.

Name	m _{RPD} [mmol]	m _{TREN} [mmol]	m _{diamine} [mmol]	Bulk density [mg/cm ³] ^{a)}	Skeletal density [mg/cm ³] ^{b)}	porosity [%]
RPA-1	1.91	0.64	MDA 0.96	132.2	1334.9	90.1
RPA-2	1.91	0.64	PDA 0.96	128.8	1267.8	89.8
RPA-3	1.91	0.64	DETA 0.96	126.7	1256.6	89.9
RPA-4	1.91	1.28	-	125.8	1212.9	89.6

^{a)} Bulk density was calculated through dividing mass by volume; ^{b)} Skeletal density was measured by an ULTRAPYC 1200e automatic density analyzer. Porosity= (Skeletal density - Bulk density)/ Skeletal density * 100%.

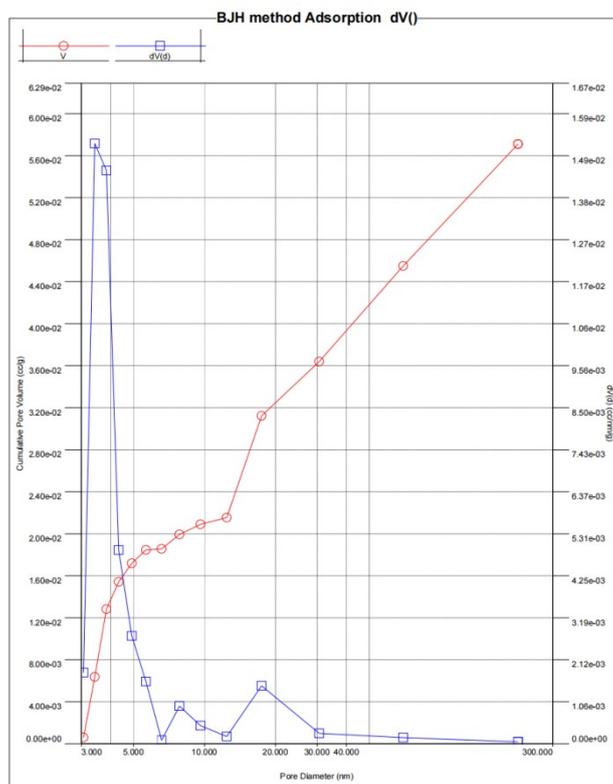


Figure S17. BJH pore size distribution of RPA-1.

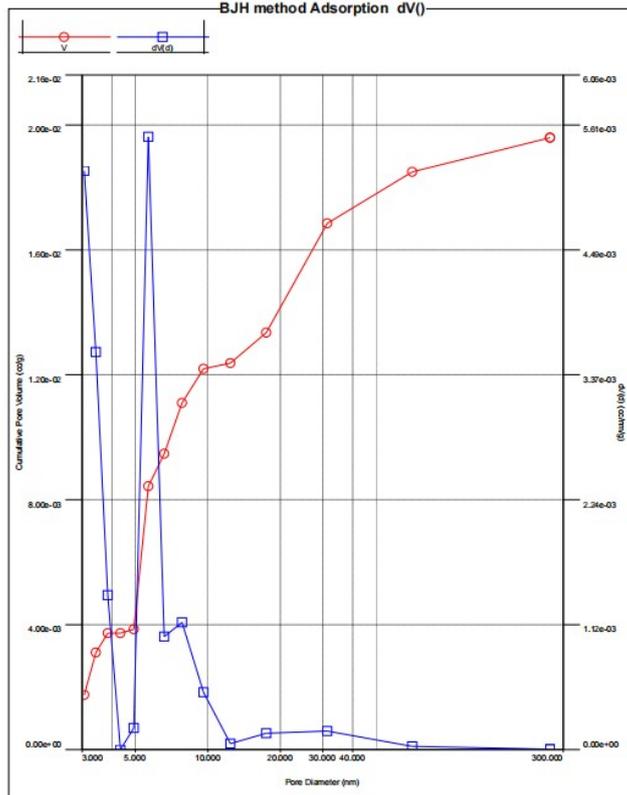


Figure S18. BJH pore size distribution of RPA-2.

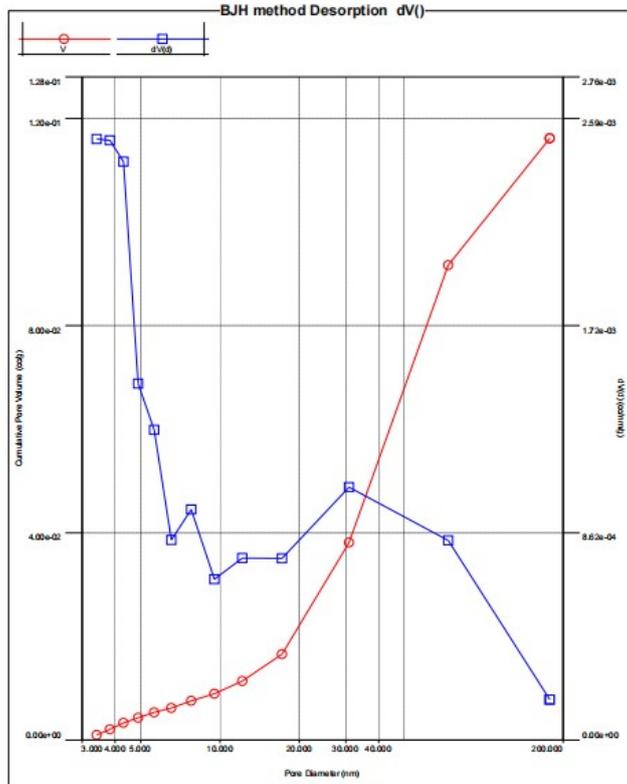


Figure S19. BJH pore size distribution of RPA-3.

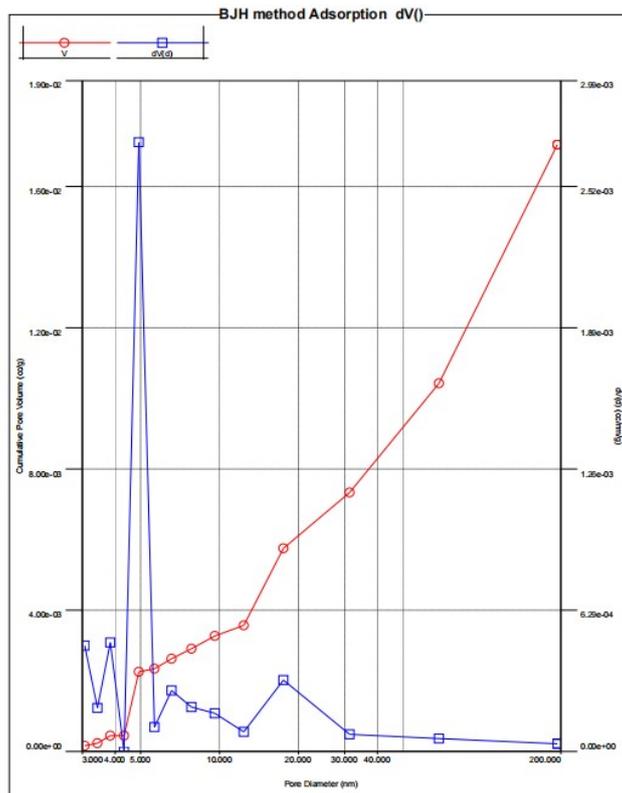


Figure S20. BJH pore size distribution of RPA-4.

Table S 2 Microstructure and Thermal properties of RPAs.

Name	Surface area [m ² /g] ^{a)}	Average pore diameter [nm] ^{b)}	Thermal conductivity [W/m·K] ^{c)}
RPA-1	52.30	4.56	0.0302
RPA-2	23.07	3.73	0.0304
RPA-3	18.00	26.74	0.0193
RPA-4	6.35	11.39	0.0136

a) Surface area was calculated based on BET theory; b) Average pore diameter was calculated using BJH method; c) Thermal conductivity was calculated using this formula: γ (thermal conductivity) = K (thermal diffusivity) · ρ (density) · c (specific heat capacity). Thermal diffusivity was measured by hyperflash flash diffusivity thermal analyzer. Specific heat capacity was measured by differential scanning calorimetry.

3.5 Acid hydrolysis recycling of r-PET aerogel

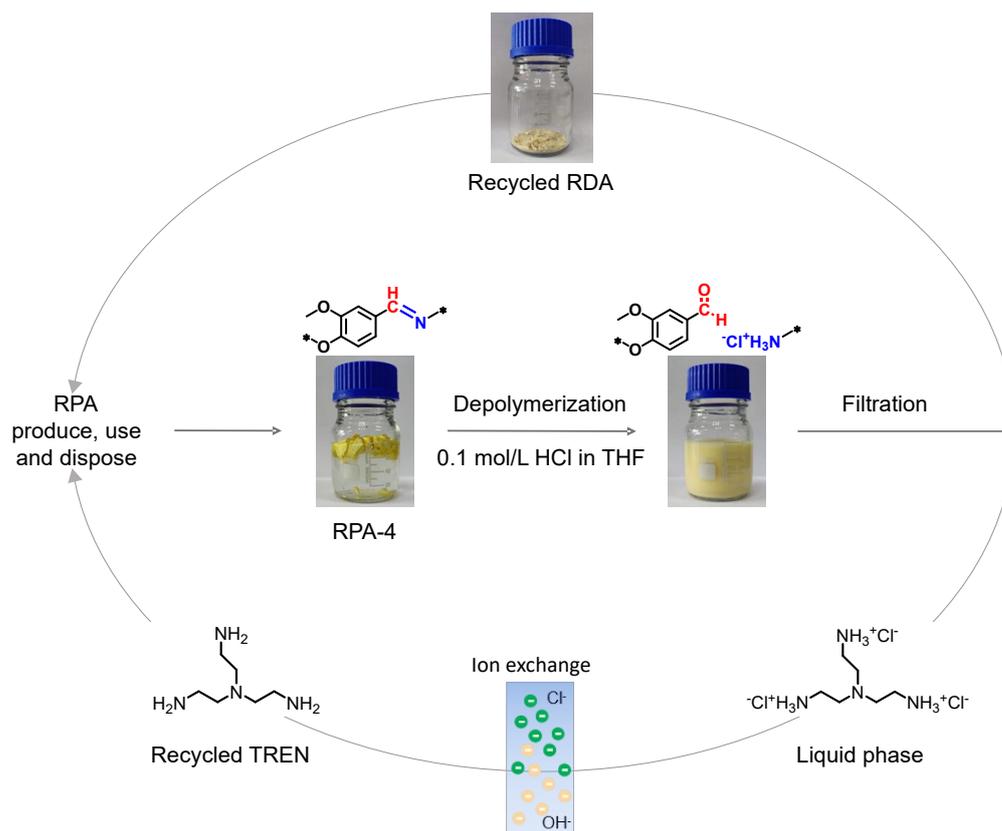


Figure S21. Complete closed-loop recycling scheme for RPA-4. The imine bond in RPA-4 can be completely dissociated under acidic conditions. The obtained RDA and TREN hydrochloride can be separated and recycled through filtration and simple sorting. TREN hydrochloride can be recovered through ion exchange resin to obtain TREN. The RDA recycling rate is over 95% and the TREN recycling rate is over 90%.

4. Reference

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