Facile upcycling of poly (bisphenol A carbonate) via dynamic covalently cross-linking networks

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Supporting information

1. Raw materials and acronyms

Table S 1. Explanation of acronyms used in this work

Acronyms	Materials
PC	Poly (bisphenol A carbonate, PC)
CDs	Compact discs
WPC	Waste polycarbonate
BPA	Bisphenol A
TTDI	Trimer of toluene-2,4-diisocyanate
OCI	The product directly obtained through transesterification between BPA and PC
OCII	OCI was treated with ethanol to remove excess BPA
OCD	Oligomers (from waste CDs)
OCI-T	OCI cross-linked with TTDI
OCII-T	OCII cross-linked with TTDI
BP-T	BPA cross-linked with TTDI
OCD-T	OCD cross-linked with TTDI

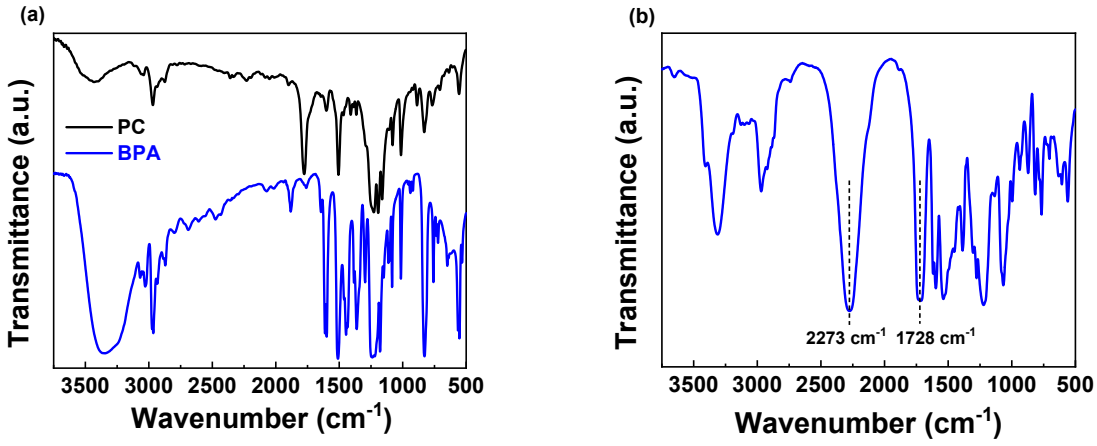


Figure S 1. FTIR spectra of (a) PC and BPA; (b) TTDI.

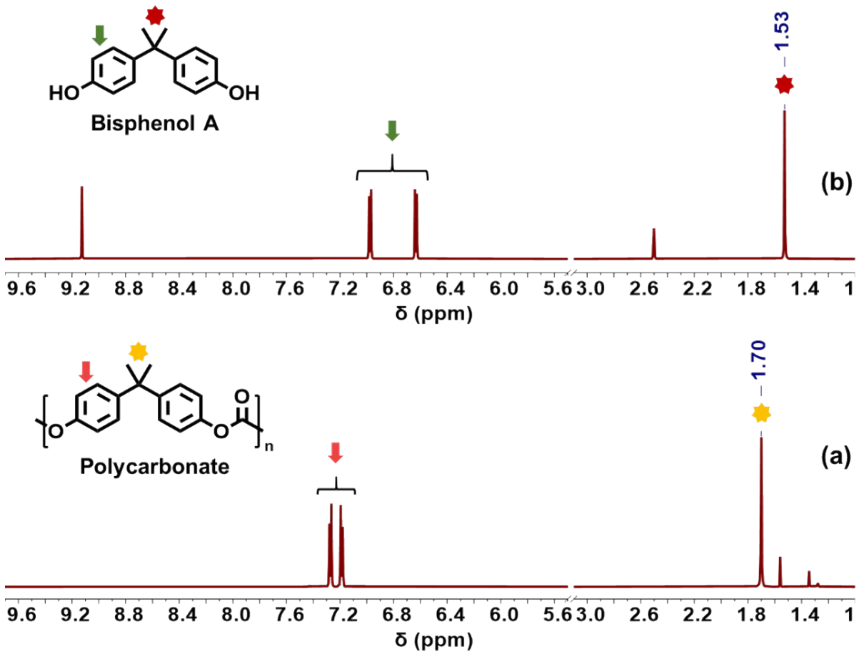


Figure S 2. ^{1}H NMR spectra of (a) PC, and (b) BPA.

2. PC degradation

2.1 Synthesis and characterization of oligomers (OCI and OCII)

In a typical synthesis, a mass ratio of 0.228:1 of BPA to PC was employed. PC 19.5 g was dissolved in 130 mL of THF to obtain a clear solution, into which 4.452 g of BPA and 0.465 g of $Ca(acac)_2$ were added. The mixture was transferred to a Teflon-lined hydrothermal reactor and heated at 180 °C for 9 h. The reaction mixture was centrifuged at 10000 rpm for 10 min to remove the catalyst, and the obtained solution was dried in a vacuum oven at 60 °C after solvent evaporation. The final product was designated as OCI. The detailed composition of the raw materials used in the synthesis is provided in Table S2.

To remove low molecular weight fragments and excess BPA, the OCI was continuously stirred with ethanol for 2 h followed by filtration and washed twice with ethanol. The filtrate was dried in a vacuum oven until a constant weight was achieved, and the product was obtained as OCII with high molecular weight.

Table S 2. Specific composition and conditions for OC synthesis

PC (g)	BPA (g)	BPA:PC Mass ratio	$Ca(acac)_2$ (g)	THF (ml)	Temperature (°C)	Time (h)
19.5	4.452	0.228:1	0.465	130	180	9

Figure S 3. Photograph of the product OCI.

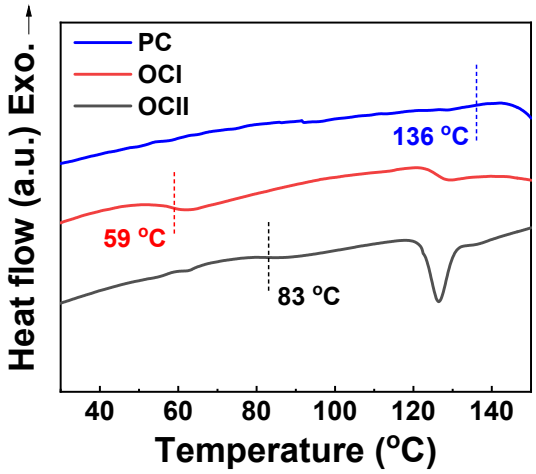


Figure S 4. DSC curves of PC, OCI, and OCII (N_2 atmosphere, heating rate: 10 °C·min^{-1}).

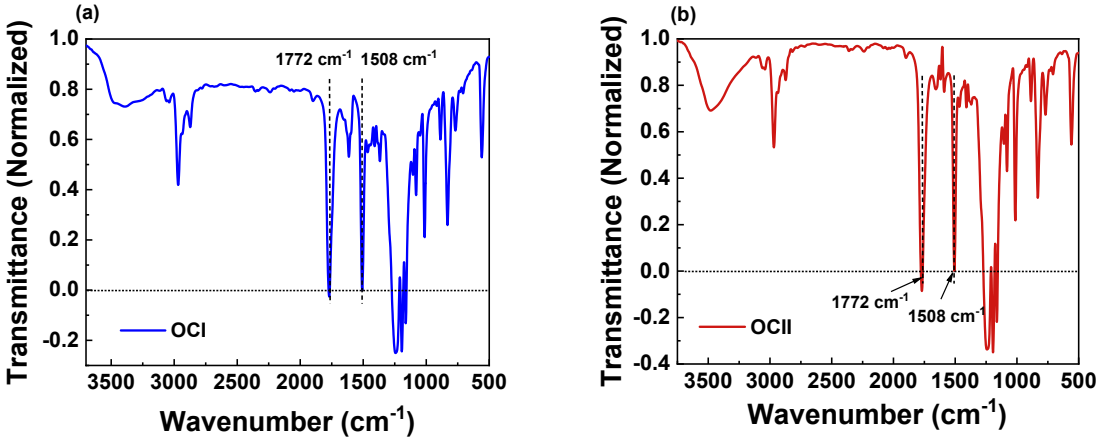
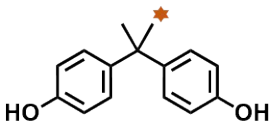


Figure S 5. FTIR of (a) OCI and (b) OCII (plotted based on the normalized intensity of benzene ring peak at 1508 cm^{-1}).

The number-average molecular weight (M_n) was calculated via ^1H NMR end-group analysis by integrating the signals of methyl proton belong to free BPA (1.53 ppm), monocarbonated BPA (chain-end, 1.60 ppm) and dicarbonated BPA (1.67 ppm) species in the region.

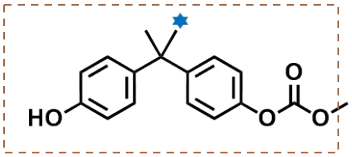
Table S 3. The mole fraction (calculated from NMR spectrum) and theoretical molecular weight of the species in OCI.

Sample	Free BPA	Monocarbonated BPA (1-BPA)	Dicarbonated BPA (2-BPA)
Chemical shift(δ, ppm)	1.53	1.60	1.67
Molecular weight($g \cdot mol^{-1}$)	228.29	271.29	254.08
Integrated peak area	1.00	5.46	6.12
Mole fraction	0.079	0.434	0.486



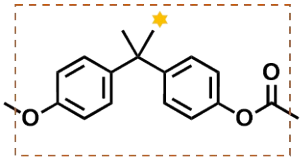
BPA

M_w=228.29



Monocarbonated bisphenol A

M_w=271.29



Dicarbonated bisphenol A

M_w=254.08

The total numbers of molecules can be considered as the sum of number of BPA and the number of oligomers, where the number of oligomers was determined by dividing the number of end groups (monocarbonated BPA) by 2.

The M_n of OCI was calculated as:

$$M_n = \frac{f_{BPA} * M_{BPA} + f_{1-BPA} * M_{1-BPA} + f_{2-BPA} * M_{2-BPA}}{\frac{f_{1-BPA}}{2} + f_{BPA}}$$

$$M_n = \frac{0.079 * 228.29 + 0.434 * 271.29 + 0.486 * 254.08}{\frac{0.434}{2} + 0.079} = 875.8 \ g \cdot mol^{-1}$$

Where, f_{BPA}, f_{1-BPA}, and f_{2-BPA} represent the mole fraction of free BPA, monocarbonated BPA and dicarbonated BPA. M_{BPA}, M_{1-BPA}, and M_{2-BPA} represent the corresponding molecular weight of the repeat units.

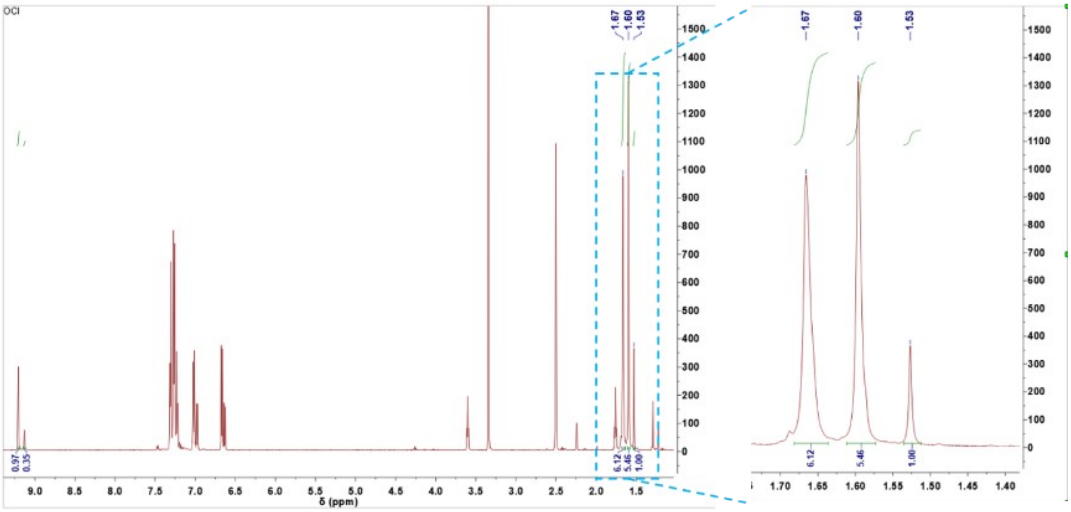


Figure S 6. The ^{1}H NMR spectrum of OCI (DMSO-d_6).

Similarly, the M_n of OCII was calculated as:

$$M_n = \frac{0.015 * 228.29 + 0.287 * 271.29 \ + 0.698 * 254.08}{\frac{0.287}{2} + 0.015} = 1628.1 \quad g \cdot mol^{-1}$$

Table S 4. The mole fraction (calculated from NMR spectrum) and theoretical molecular weight of the species in OCII.

Sample	Free BPA	Monocarbonated BPA (1-BPA)	Dicarbonated BPA (2-BPA)
Chemical shift(δ, ppm)	1.53	1.59	1.66
Molecular weight($g \cdot mol^{-1}$)	228.29	271.29	254.08
Integrated peak area	1.00	18.75	45.56
Mole fraction	0.015	0.287	0.698

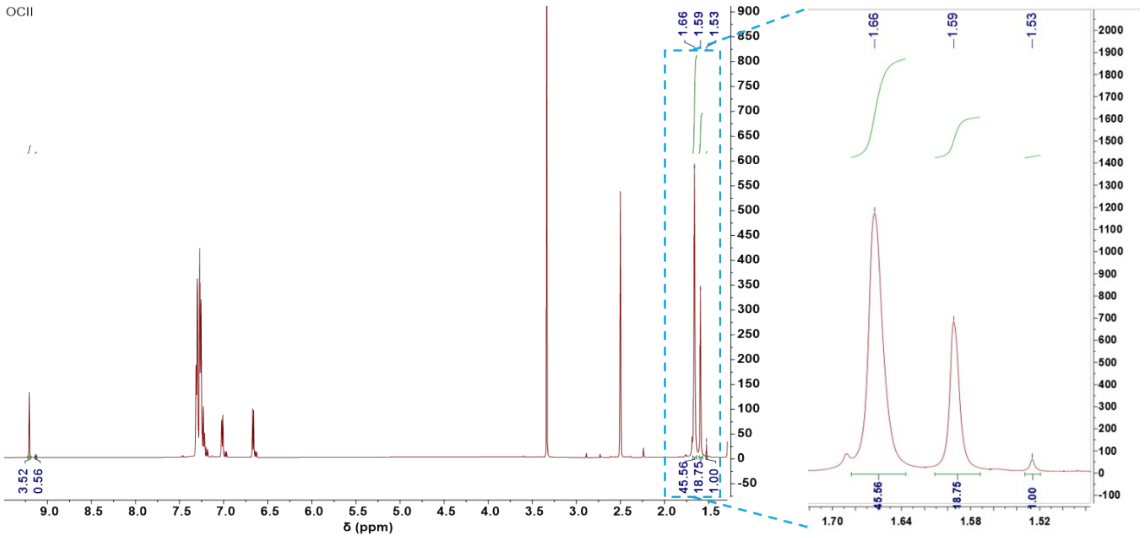


Figure S 7. The ^{1}H NMR spectra of OCII (DMSO-d_6).

2.2 Waste PC degradation

The wasted CDs were cut into small pieces and immersed in 10 wt% aqueous NaOH at room temperature for 24 h to remove the lacquer coatings. The remaining PC fragments were rinsed three times with deionized water, dried in a vacuum oven to constant weight. Subsequently, the PC fragments were degraded via transesterification with BPA, using a procedure similar to that described in section 2.1. The detailed reaction condition is given in Table S 3 and the resulting products as noted as OCD.

Table S 5. Reaction conditions for waste CD degradation

Wasted CDs (g)	BPA (g)	BPA:PC Mass ratio	$Ca(acac)_2$ (g)	THF (ml)	Temperature (^{o}C)	Time (h)
19.5	3.11	0.159:1	0.465	130	180	9

The compositions and molecular weights of the samples were determined using an Agilent 1260 gel permeation chromatography (GPC) system with a PLgel Mixed-B and a PLgel Mixed-C columns at 35°C, employing tetrahydrofuran as the eluent at a flow rate of 1 mL·min^{-1}. The standard polymer used for GPC equipment calibration was Poly (methyl methacrylate).

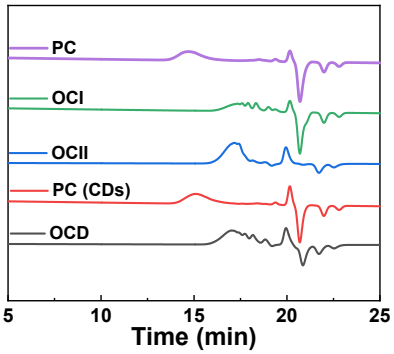


Figure S 8. GPC analysis of pristine PC, OCI, OCII, PC (CDs), and OCD.

Table S 6. Results of GPC analysis

Samples	M_n (g·mol^{-1})	M_w (g·mol^{-1})	Polydispersity
PC	29966	52392	1.75
OCI	1032	2038	1.98
OCII	2200	3355	1.52
PC (CDs)	19051	33369	1.76
OCD	1509	3040	2.01

3. Formation and characteristics of dynamic crosslinking networks

3.1 Composition and properties of OCI-T

Since the OCI contained polymer fragments along with residual BPA, the series of OCI-T*x* polymers was synthesized with varying concentrations of TTDI. The crosslinking density was found to be optimal in the sample OCI-$T_{1.05}$, which displayed the highest T_g and tensile properties among the series.

Table S 7. Reactants feeding ratios for the synthesis of OCI-T

OCI-T*x*	OCI (g)	TTDI (g)	TTDI/OCI (mass ratio)
OCI-$T_{0.45}$	4.0	1.80	0.45:1
OCI-$T_{0.75}$	4.0	3.00	0.75:1
OCI-$T_{0.90}$	4.0	3.60	0.90:1
OCI-$T_{1.05}$	**3.0**	**3.15**	**1.05:1**
OCI-$T_{1.20}$	2.8	3.36	1.20:1
OCI-$T_{1.35}$	2.7	3.64	1.35:1
OCI-$T_{1.50}$	2.5	3.75	1.50:1

OCI-T$_{1.65}$	2.5	4.12	1.65:1
OCI-T$_{1.87}$	2.5	4.68	1.87:1

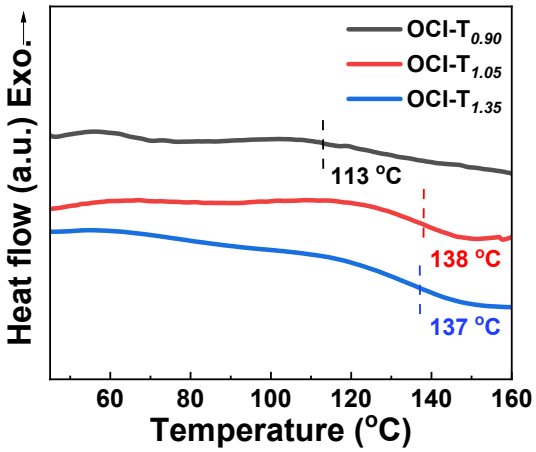


Figure S 9. DSC curves of OCI-T samples (N_2 atmosphere, heating rate: 10 °C·min^{-1}).

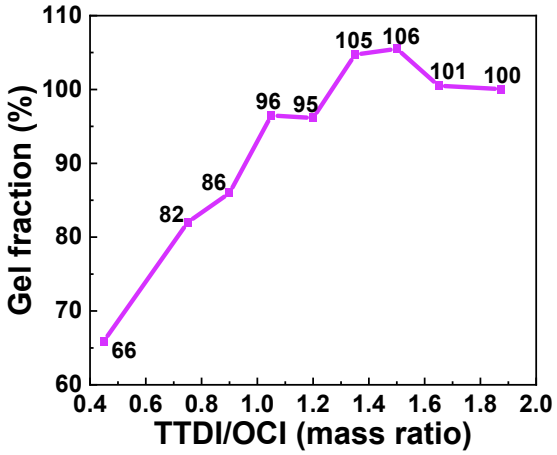


Figure S 10. Gel fraction of OCI-T samples.

3.2 Composition and properties of OCII-T

After removing the small molecular weight fragments and residual BPA from OCI, the resulting OCII, with long-chain fragments, was subjected to crosslinking using different mass ratios of TTDI to OCII. The optimal cross-linked OCII-T$_{0.60}$ was subsequently identified with high Tg and tensile strength.

Table S 8. Reactants feeding ratios for the synthesis of OCII-T

OCII-T*y*	OCII (g)	TTDI (g)	TTDI/OCII (mass ratio)

OCII-$T_{0.45}$	4.0	1.80	0.45:1
OCII-$T_{0.60}$	**4.0**	**2.40**	**0.60:1**
OCII-$T_{0.75}$	3.5	2.63	0.75:1
OCII-$T_{0.90}$	3.5	3.15	0.90:1

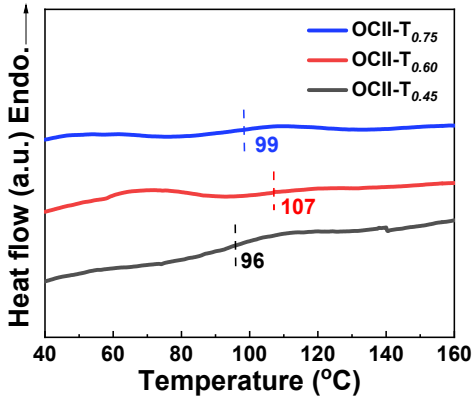


Figure S 11. DSC curves of OCII-T samples (N_2 atmosphere, heating rate: 10 °C·min^{-1}).

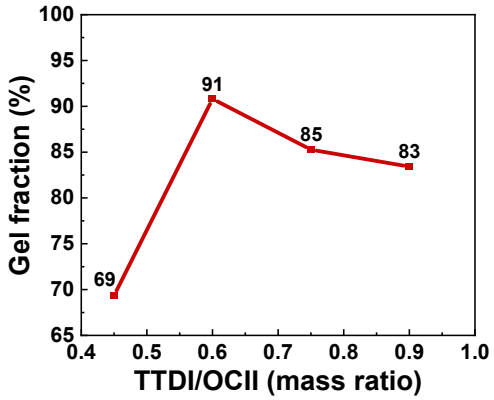


Figure S 12. Gel fraction of OCII-T samples.

3.3 Composition and properties of BP-T

BPA was also cross-linked with different dosages of TTDI, and the resulting highly cross-linked samples, BP-T*z*, were evaluated for their mechanical and thermal properties. The BP-$T_{2.1}$ exhibited the highest tensile strength (88 MPa) and (T_g, 97 °C) among different samples.

Table S 9. Reactants feeding ratios for the synthesis of BP-T

BP-T*z*	-NCO/-OH (molar ratio)	BPA (g)	TTDI (g)	TTDI/BPA (mass ratio)
BP-$T_{1.5}$	0.72:1	3.0	4.50	1.5:1

BP-$T_{1.9}$	0.90:1	3.0	5.63	1.9:1
BP-$T_{2.0}$	0.98:1	3.0	6.08	2.0:1
BP-$T_{2.1}$	**1:1**	**3.0**	6.30	**2.1:1**
BP-$T_{2.2}$	1.05:1	3.0	6.53	2.2:1

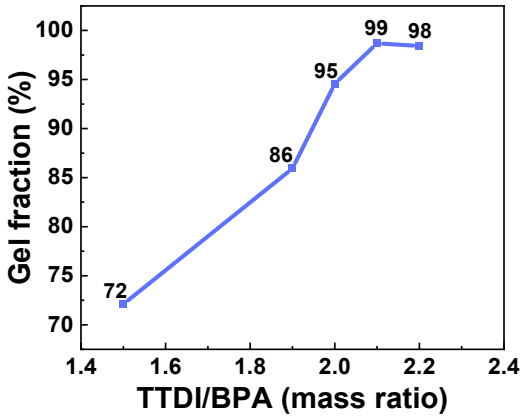


Figure S 13. Gel fraction percentages of BP-T samples.

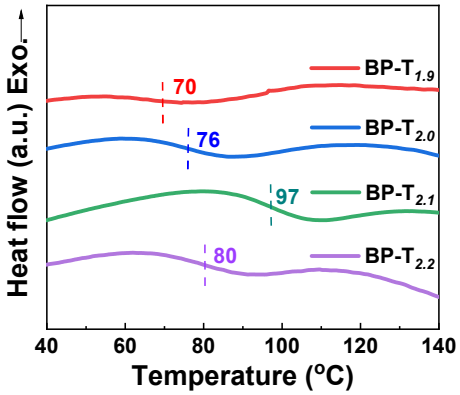


Figure S 14. DSC curves of BP-T samples (N_2 atmosphere, heating rate: 10 °C·min^{-1}).

3.4 Properties of dynamic crosslinking networks

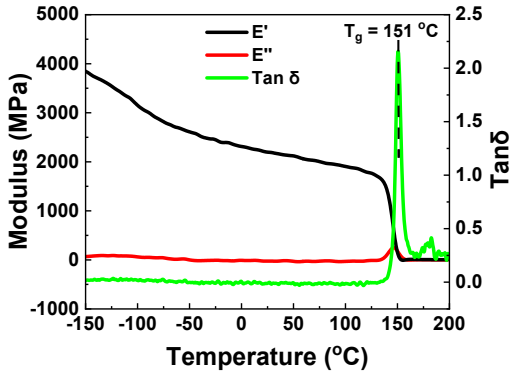


Figure S 15. DMA analysis of original PC (heating rate: 3 °C·min^{-1}).

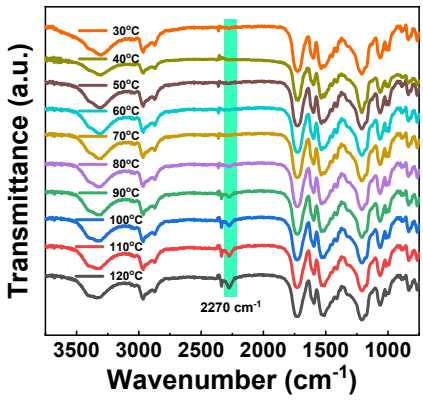


Figure S 16. *In-situ* temperature-dependent FTIR spectra of BP-$T_{2.1}$.

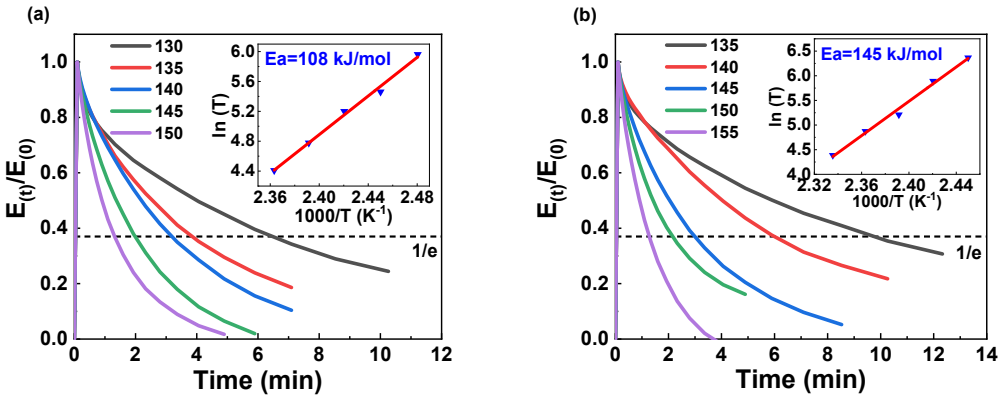


Figure S 17. Stress relaxation of (a) OCI-$T_{0.90}$ and (b) OCI-$T_{1.20}$ samples (0.5% strain).

3.5 Mechanical Properties

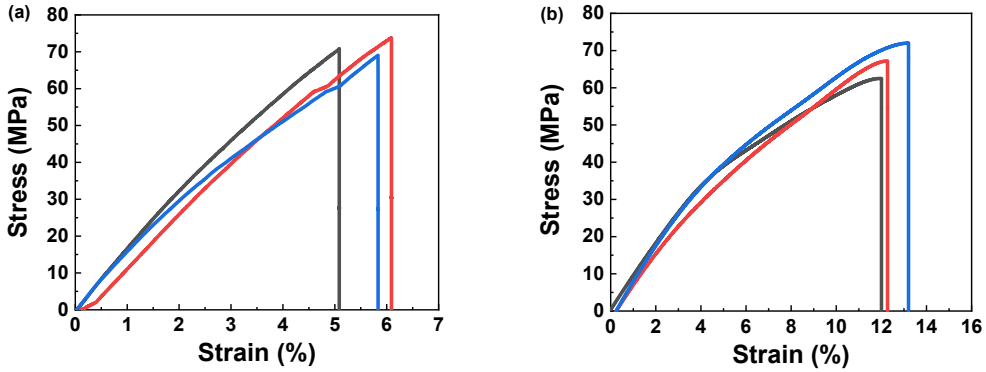


Figure S 18. Tensile properties (a) Original OCI-$T_{1.05}$; (b) Pristine PC.

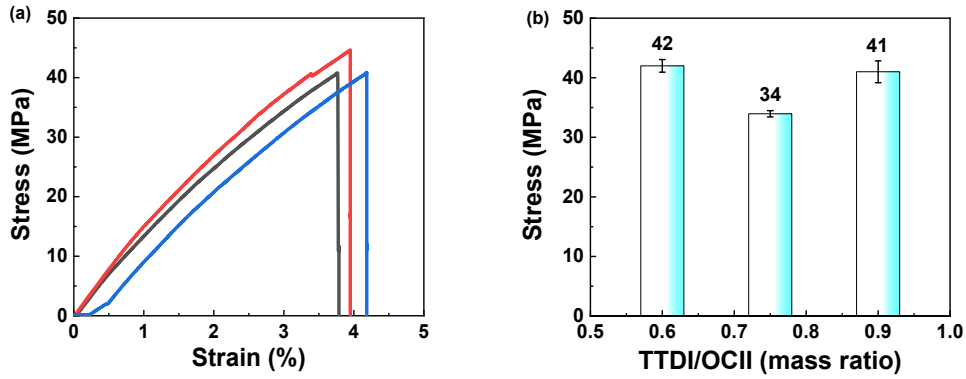


Figure S 19. (a) Tensile stress-strain curves of OCII-$T_{0.60}$ and (b) Tensile strength of OCII-T with different mass ratios of TTDI to OCII.

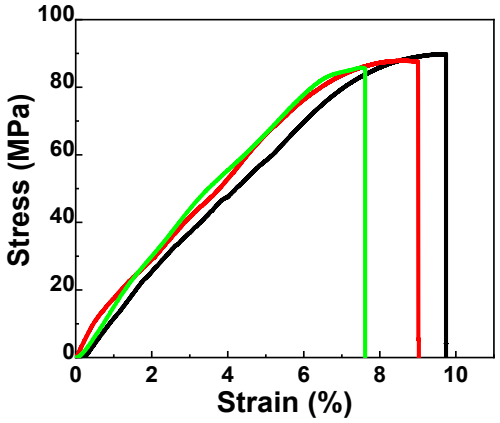


Figure S 20. Tensile properties of BP-$T_{2.1}$ optimal ratio.

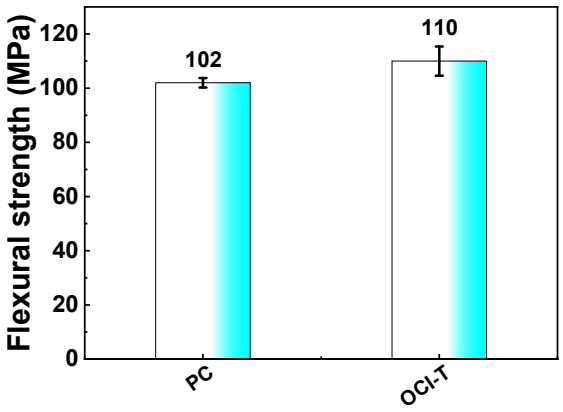


Figure S 21. Flexural strength of PC and OCI-$T_{1.05}$.

Table S 10. Flexural strength results of PC and OCI-$T_{1.05}$

Sample	Parallel testing	Flexural strength (MPa)	Average (MPa)
PC	1	104.06	102±2
	2	101.12	
	3	99.89	
OCI-$T_{1.05}$	1	112.08	110±5
	2	106.54	
	3	111.62	

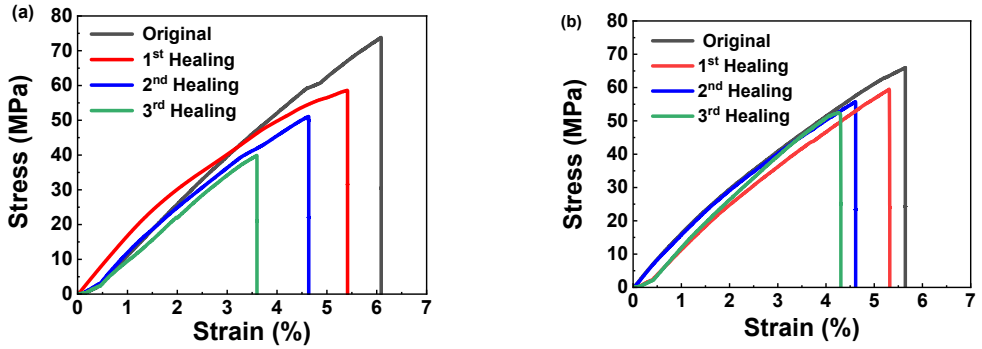


Figure S 22. Tensile properties of (a) OCI-$T_{1.05}$ and (b) OCI-$T_{1.35}$ after reprocessing

Table S 11. Mechanical properties and recycling conditions of reported recycling of polycarbonate

Tensile Strength (MPa)	Elongation at break (%)	Recycling conditions	Basic structure	Ref.

75.8-79.4	3.1-3.8	240 °C, 10 MPa, 2h	Poly(carbonate-imine)	[1]
15-25	13-3.4	240 °C, 10 MPa, 1h	Poly(carbonate-imine)	[2]
46	4.3	200 °C, 10 MPa, 1h	Poly(carbonate-acetal)	[3]
14.9	3115	120 °C, 30 MPa, 1h	Polyurethane	[4]
71	9.5	Depolymerization at 120 °C	Poly(bisphenol A carbonate) into an epoxy-curing agent	[5]
72	5.7	160 °C, 18 MPa, 2 h	Polyurethane	This work

3.6 Structure stability

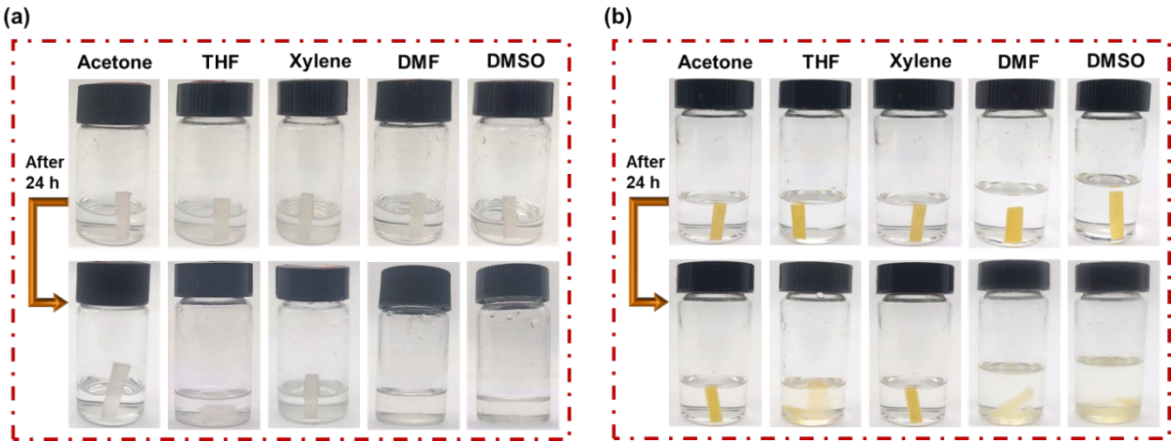


Figure S 23. Solvent resistant properties of (a) BP-$T_{2.1}$ and (b) OCII-$T_{0.60}$ by immersing in different solvents.

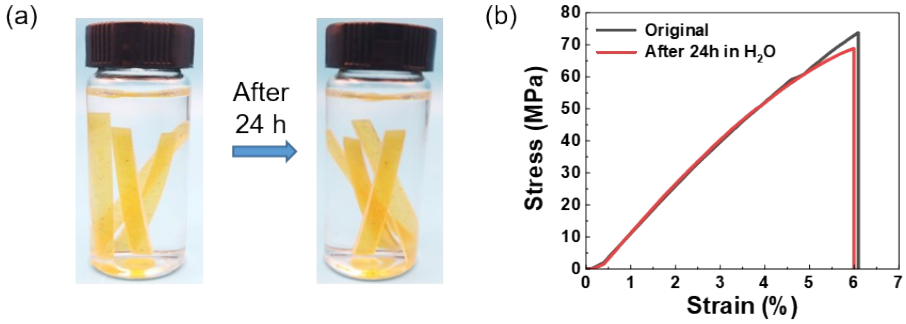


Figure S 24. (a) Appearance of OCI-$T_{1.05}$ sample immersed in water for 24 h. (b) Typical tensile curves of OCI-$T_{1.05}$ before and after 24 h of water immersion.

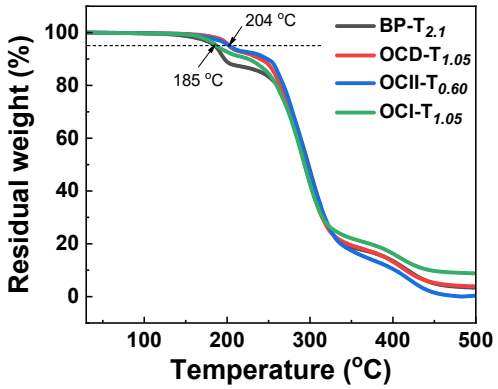


Figure S 25. TGA curves of different cross-linked samples (heating rate: 10 °C·min^{-1}).

4. Composition and properties of OCD-T

The oligomers (OCD) derived from wasted CDs, possessing a composition similar to that of OCI and containing polymer fragments with residual BPA, was also cross-linked using varying amounts of TTDI. Among the formulations, OCD-T$_{1.05}$ exhibited the optimal crosslinking ratio and demonstrated superior mechanical properties.

Table S 12. Reactants feeding ratios for the synthesis of OCD-T

OCD-T*x*	OCD (g)	TTDI (g)	TTDI/OCD (mass ratio)
OCD-T$_{0.75}$	3.0	2.25	0.75:1
OCD-T$_{0.90}$	3.0	2.70	0.90:1
OCD-T$_{1.05}$	**3.0**	**3.15**	**1.05:1**
OCD-T$_{1.20}$	3.0	3.60	1.20:1
OCD-T$_{1.35}$	3.0	4.05	1.35:1

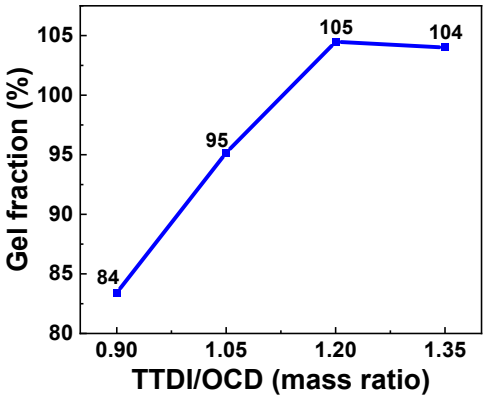


Figure S 26. Gel fraction percentages of OCD-T samples.

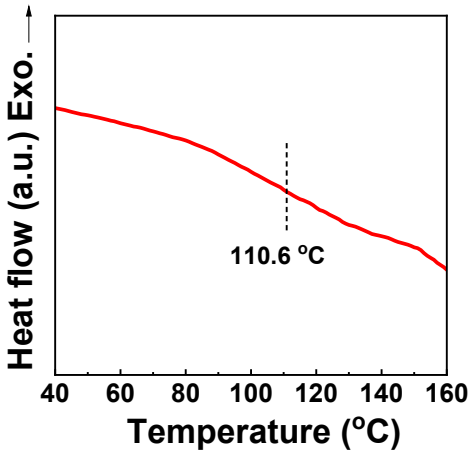


Figure S 27. DSC curve of OCD-$T_{1.05}$ (N_2 atmosphere, heating rate: 10 °C·min^{-1}).

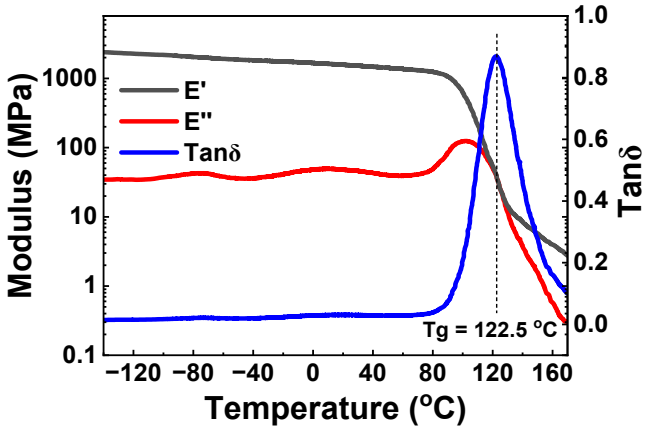


Figure S 28. DMA curves of OCD-$T_{1.05}$ measured at heating rate 3 °C·min^{-1}.

5. OCI-T based Composites

Table S 13. Flexural strength results of PC and OCI-T and composites

Sample	Parallel testing	Flexural strength (MPa)	Average (MPa)
GF_{60}/ $OCI\text{-}T_{40}$	1	122.54	118±8
	2	123.87	
	3	106.33	
GF_{60}/ $OCD\text{-}T_{40}$	1	109.73	116±6
	2	117.65	
	3	120.71	

Table S 14. ILSS results of GF_{60}/OCI-T_{40} composite

Parallel testing	ILSS (MPa)	Average (MPa)
1	11.95	
2	10.46	12±1
3	12.83	

Table S 15. Flexural strength results of CGF_{40}/OCI-T_{60} composite

Sample	Parallel testing	Flexural strength (MPa)	Average (MPa)
Original	1	61.39	65±3
	2	64.64	
	3	69.24	
Healing 1	1	49.20	47±2
	2	47.31	
	3	45.56	
Healing 2	1	39.11	37±32
	2	31.99	
	3	38.44	
Healing 3	1	34.40	35±3
	2	31.53	
	3	37.78	

References for literature comprasion:

1. Reddy, K.S.K., et al., *Upcycling Waste Polycarbonate to Poly(carbonate imine) Vitrimers with High Thermal Properties and Unprecedented Hydrolytic Stability.* ACS Sustainable Chemistry & Engineering, 2023. **11**(23): p. 8580-8591.
2. Chen, Y.-C., et al., *Upcycling of waste polycarbonate to recyclable Poly (carbonate-imines) with exceptional thermal properties and unprecedented flame retardancy.* Chemical Engineering Journal, 2024. **492**: p. 152376.

3. Chen, Y.-C., et al., *Poly(carbonate acetal) vitrimers with enhanced thermal properties and closed-loop thermal recyclability derived from waste polycarbonate-derived polyaldehyde and pentaerythritol/erythritol/d-sorbitol.* Green Chemistry, 2024. **26**(19): p. 10275-10289.
4. Chen, S.-W., et al., *A facile strategy to achieve polyurethane vitrimers from chemical recycling of poly(carbonate).* Chemical Engineering Journal Advances, 2022. **11**: p. 100316.
5. Peng, Z., et al., *The carbonate exchange reaction strategy for chemical recycling of poly(bisphenol A carbonate) into an epoxy-curing agent.* Polymer Chemistry, 2025. **16**(4): p. 465-474.