Electronic Supplementary Information

Cationic Polyurethane from CO_2-polyol as Effective Barrier Binder to Polyaniline-based Metal Anti-corrosion Material

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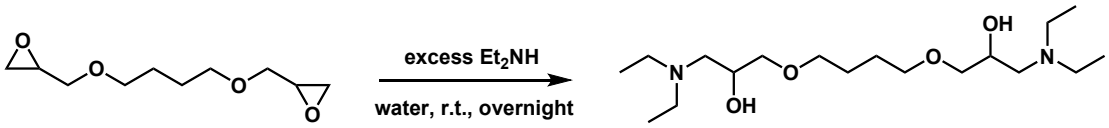
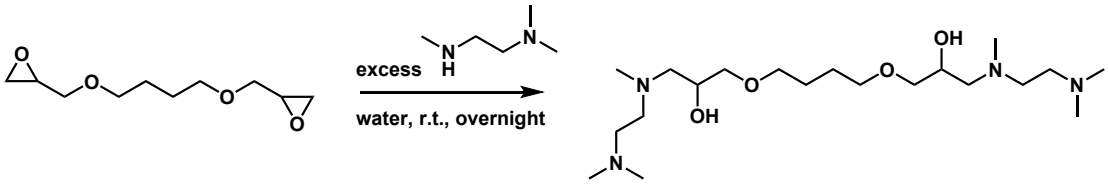
Contents

Synthesis of BDE



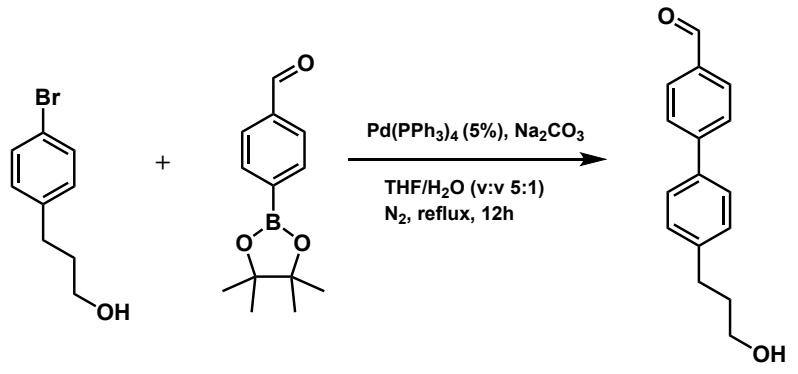
To a 250 ml single-neck round bottom flask with a magnetic stir bar was added 1,4-butanediol diglycidyl ether (16.18 g, 80 mmol), excess amount of diethylamine, and H_2O (30 ml), a yellow solution was formed upon vigorous stirring at room temperature overnight. The reaction process was monitored with thin layer chromatograph (TLC), when the 1,4-butanediol diglycidyl ether was consumed completely, another 30 ml of H_2O was added, after 10 min stirring the mixture was extracted with diethyl ether for three times (3 x 50 ml). The combined organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to afford BDE. (Yield: 95%)

Synthesis of TDTD



A similar synthesis process to BDE, the only difference is the remaining N,N,N'-Trimethylethylenediamine was removed by vacuum distillation. (Yield: 89%)

Synthesis of 4'-(3-hydroxypropyl)-[1,1'-biphenyl]-4-carbaldehyde



3-(4-bromophenyl)propan-1-ol (4.628 g, 21.52 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (4.76 g, 20.50 mmol) as well as Na_2CO_3 (22.81g, 215.2 mmol) were dissolved in 300 mL of tetrahydrofuran and 60ml H_2O. After the addition of tetrakis(triphenylphosphine)palladium (1.24g, 1.076mmol), the mixture was refluxed for 12 h.

When it was cooled to room temperature, the solution was extracted twice with dichloromethane (3 × 50 mL). The obtained organic layer was washed with plenty of water and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column to give yellow solid with 77 % yield.

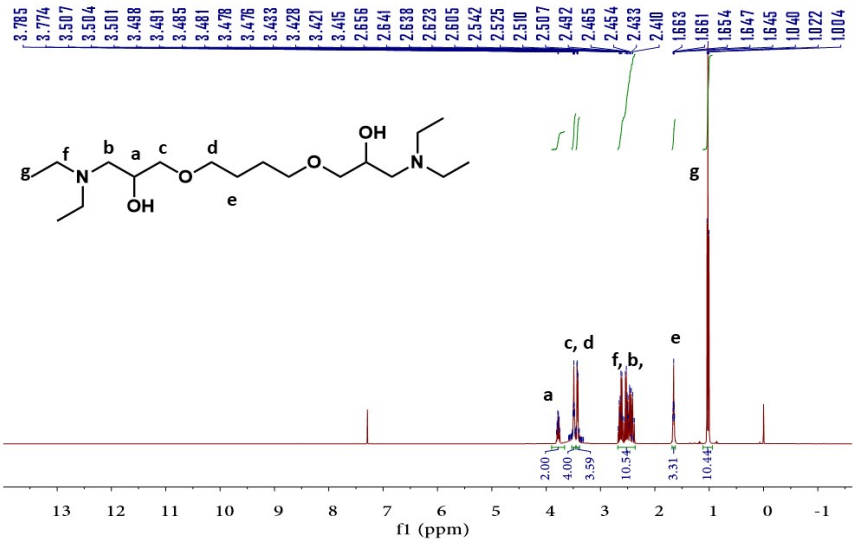


Fig. S1 The ^{1}H-NMR spectrum of BDE in $CDCl_3$.

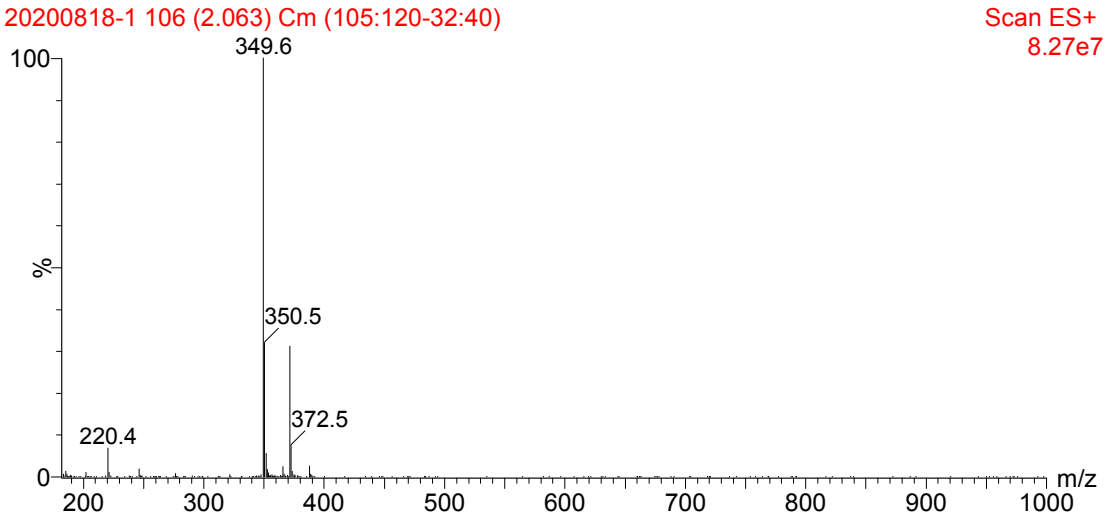


Fig. S2 The mass spectrometry of BDE in positive mode.

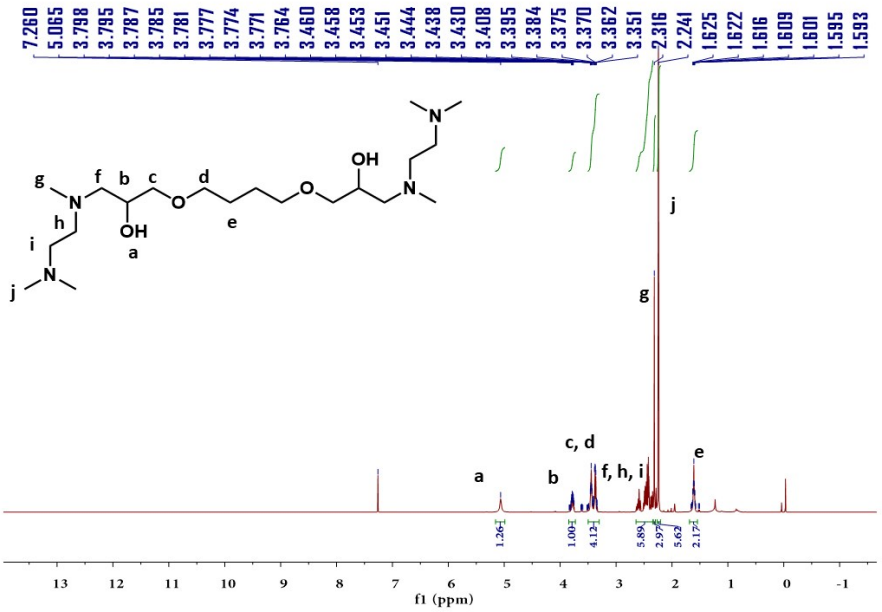


Fig. S3 The ^{1}H-NMR spectrum of TDTD in $CDCl_3$.

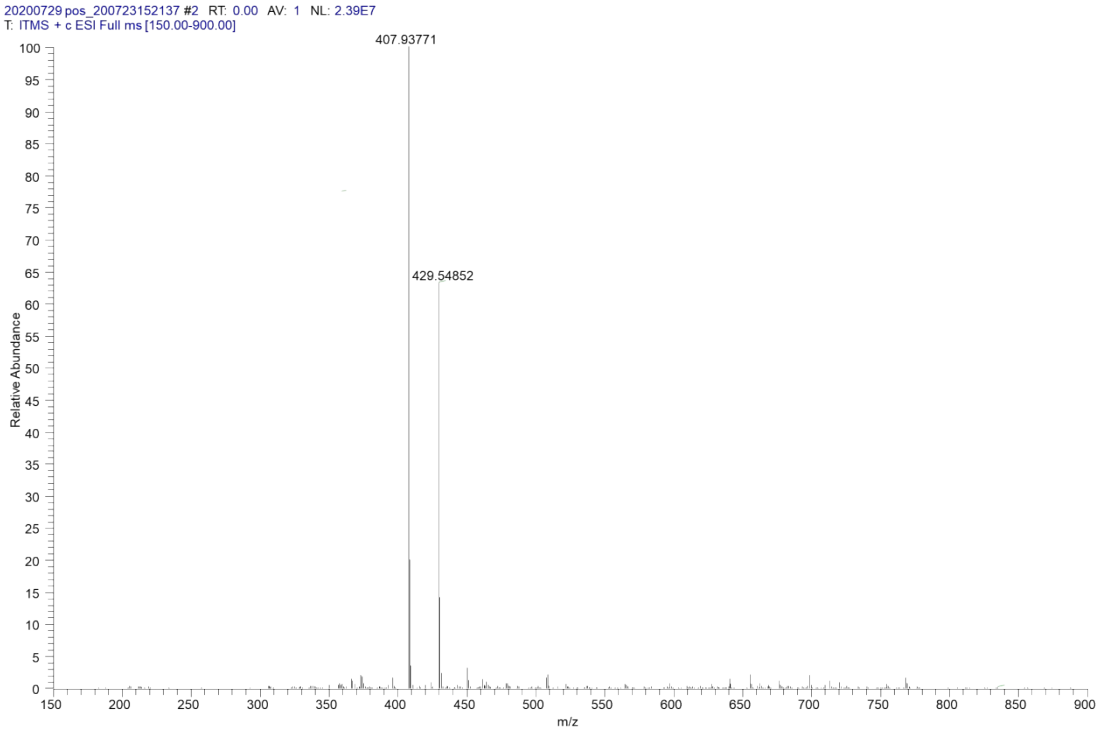


Fig. S4 The mass spectrometry of TDTD in positive mode.

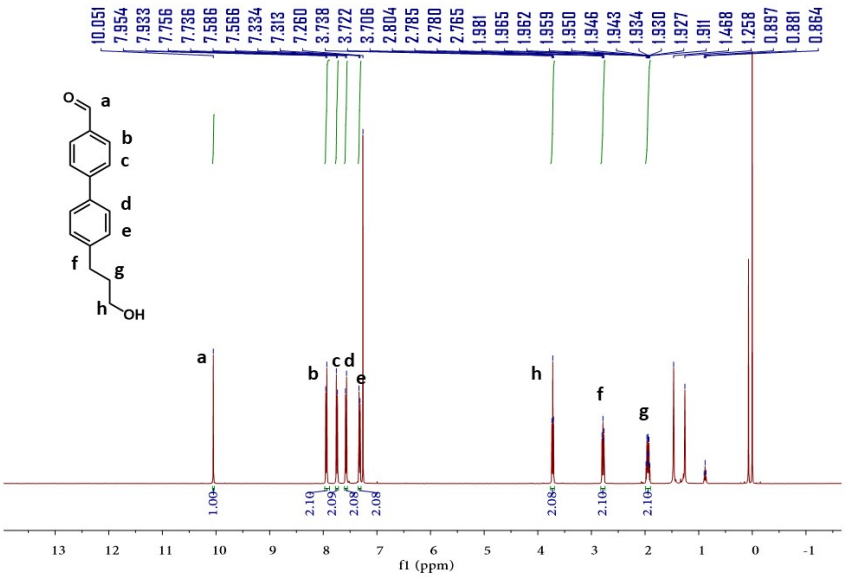


Figure S5. The ^{1}H-NMR spectrum of 4'-(3-hydroxypropyl)-[1,1'-biphenyl]-4-carbaldehyde in $CDCl_3$.

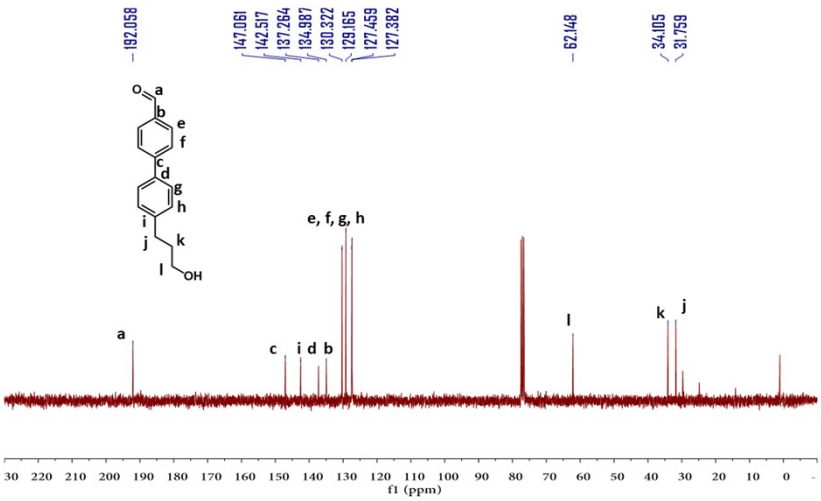


Figure S6. The ^{13}C-NMR spectrum of 4'-(3-hydroxypropyl)-[1,1'-biphenyl]-4-carbaldehyde in $CDCl_3$.

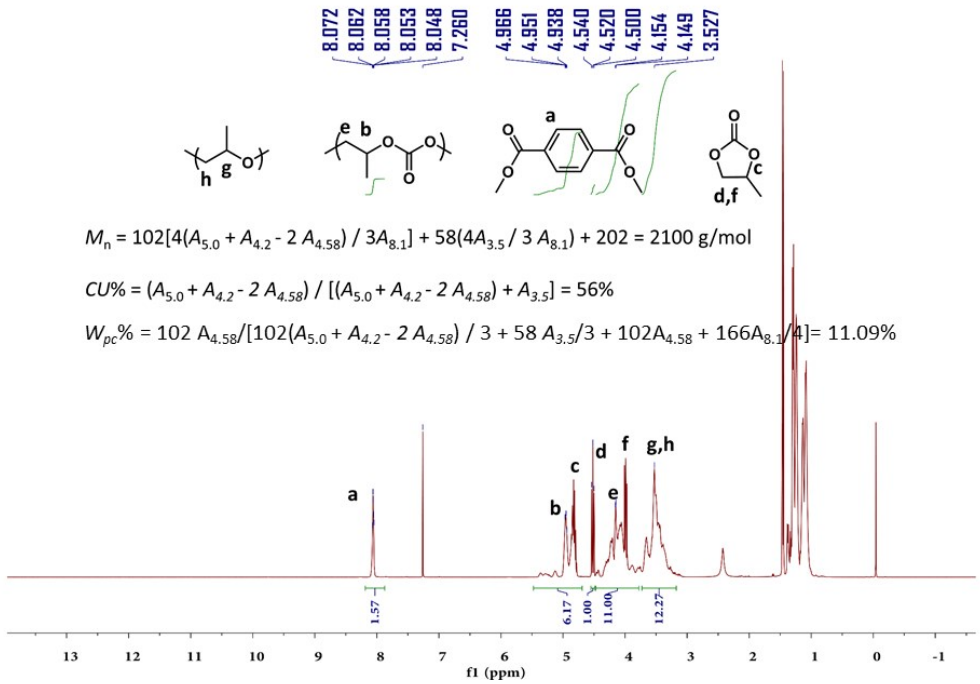


Fig. S7 The ^{1}H-NMR spectrum of CO_2-polyol in $CDCl_3$.

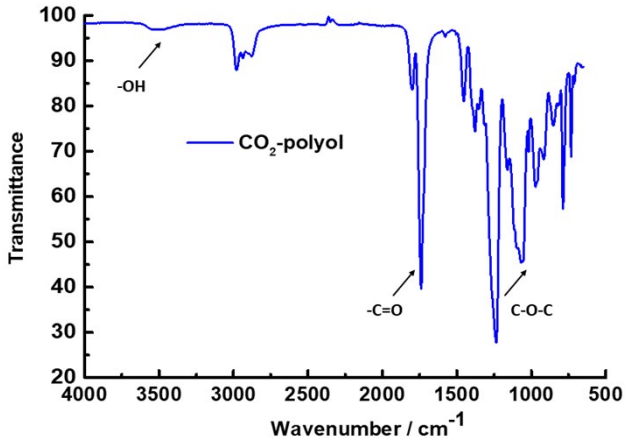


Fig. S8 The FT-IR spectrum of CO_2-polyol.

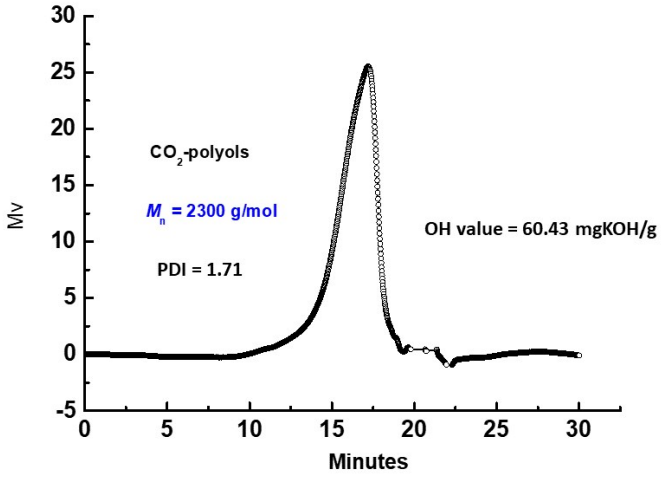


Fig. S9 The GPC spectrum of CO_2-polyol.

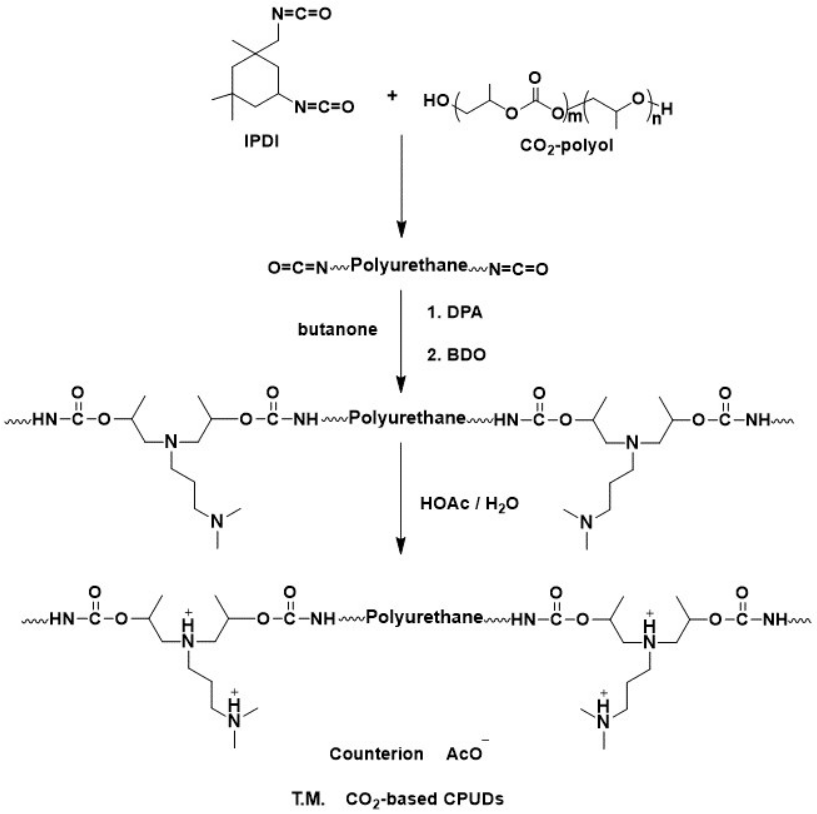


Fig. S10 Synthetic route to prepare CPUD using DPA as internal emulsifier with different neutralization degree.

Synthesis of PPC-DPA-4

Synthesized using the same method as PPC-TDTD-4.

14.31 g of PPC-diol; 6.30 g of IPDI; 0.92 g of DPA; 1.58 g of BDO; 0.51 g of HOAc

Synthesis of PPC-DPA-4(1)

Synthesized using the same method as PPC-TDTD-4.

16.20 g of PPC-diol; 7.128 g of IPDI; 1.023 g of DPA; 1.79 g of BDO; 0.28 g of HOAc

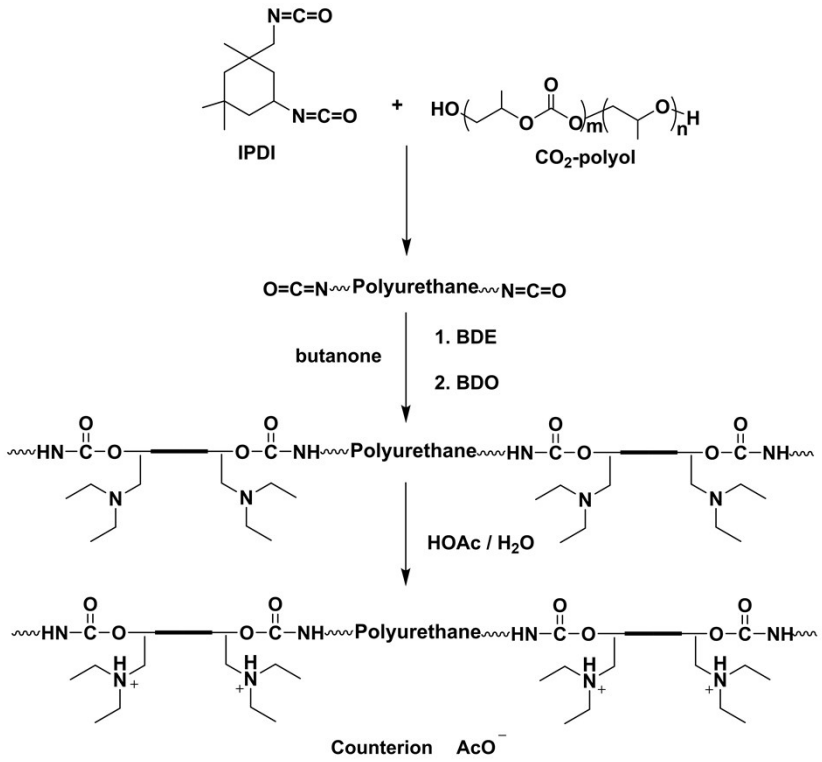


Fig. S11 Synthetic route to prepare CPUD using BDE as internal emulsifier with different neutralization degree.

Synthesis of PPC-BDE-4

Synthesized using the same method as PPC-TDTD-4.

13.40 g of PPC-diol; 5.90 g of IPDI; 0.87 g of BDE; 1.62 g of BDO; 0.30 g of HOAc

Synthesis of PPC-BDE-4(1)

Synthesized using the same method as PPC-TDTD-4.

17.10 g of PPC-diol; 7.524 g of IPDI; 1.116 g of BDE; 2.06 g of BDO; 0.19 g of HOAc

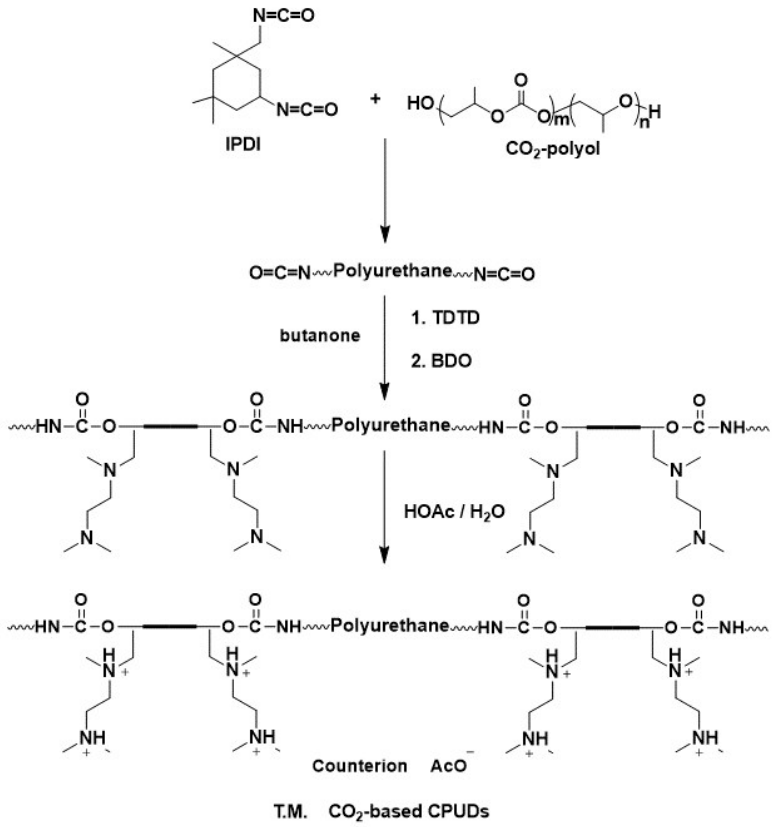


Fig. S12 Synthetic route to prepare PPC-TDTD-4(1).

Synthesis of PPC-TDTD-4(1)

Synthesized using the same method as PPC-TDTD-4.

20.10 g of PPC-diol; 8.84 g of IPDI; 1.30 g of TDTD; 2.47 g of BDO; 0.20 g of HOAc

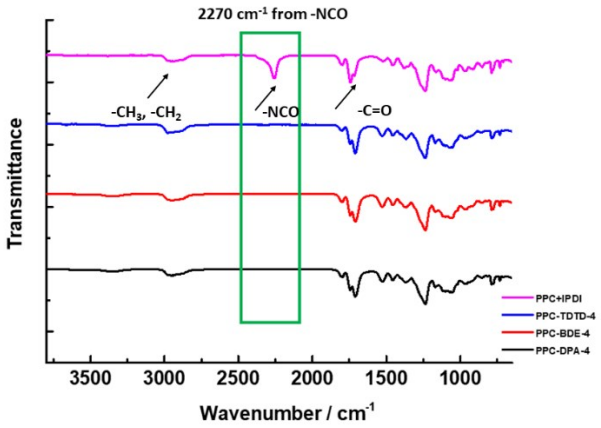


Fig. S13 FT-IR spectrum for various CPUDs.

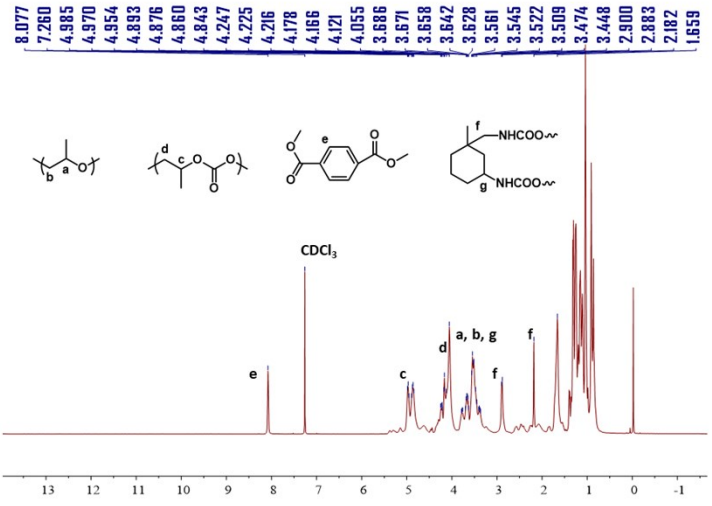


Fig. S14 [1]H-NMR spectrum of PPC-DPA-4.

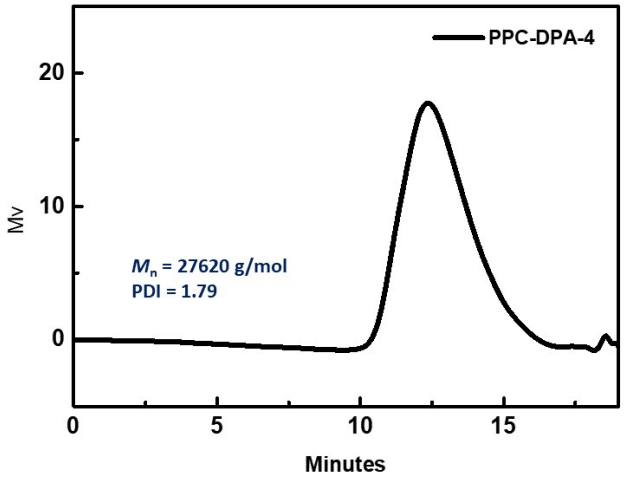


Fig. S15 GPC traces of PPC-DPA-4.

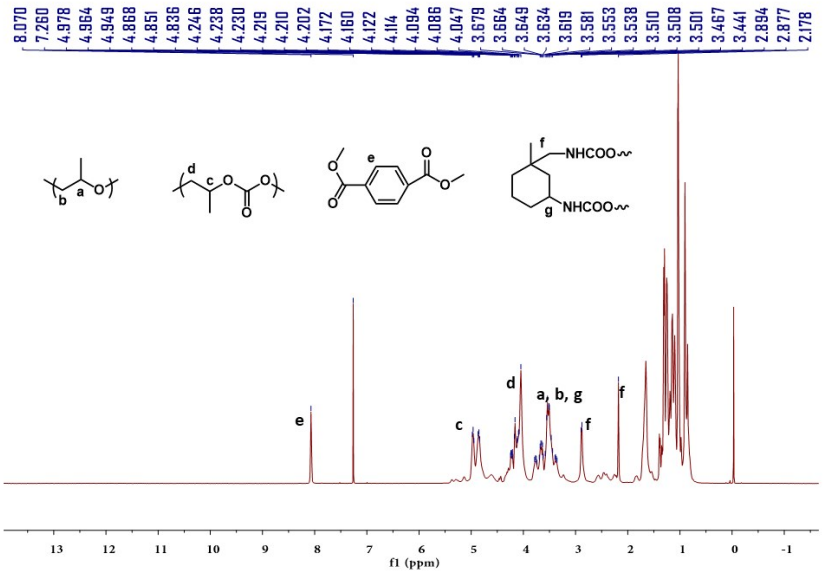


Fig. S16 ^{1}H-NMR spectrum of PPC-DPA-4(1).

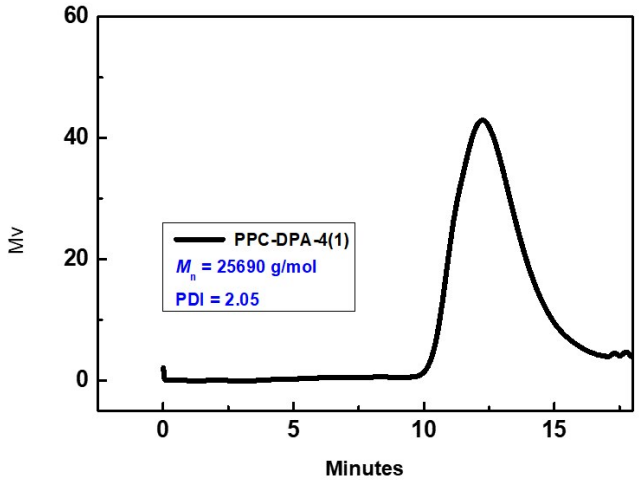


Fig. S17 GPC traces of PPC-DPA-4(1).

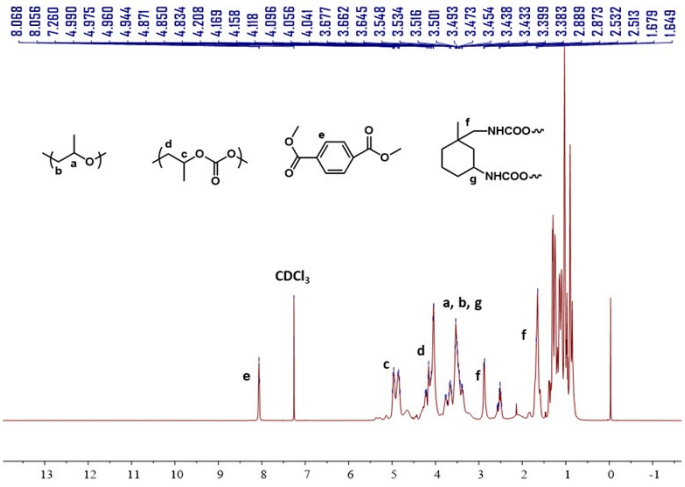


Fig. S18 [1]H-NMR spectrum of PPC-BDE-4.

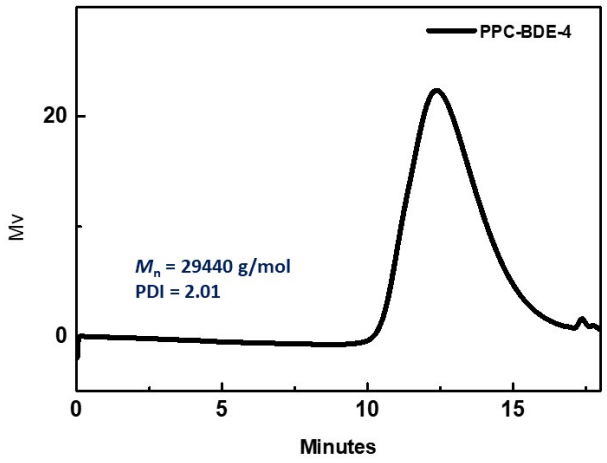


Fig. S19 GPC traces of PPC-BDE-4.

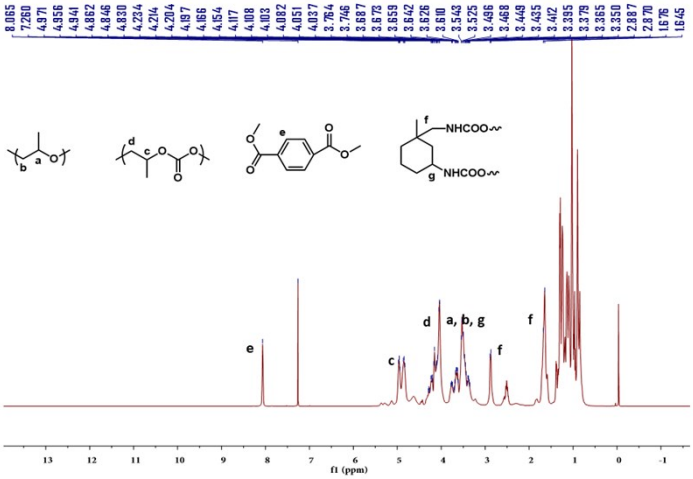


Fig. S20 ^{1}H-NMR spectrum of PPC-BDE-4(1).

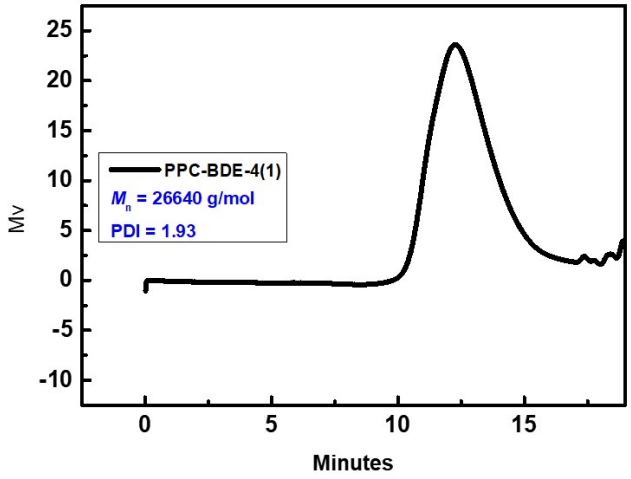


Fig. S21 GPC traces of PPC-BDE-4(1).

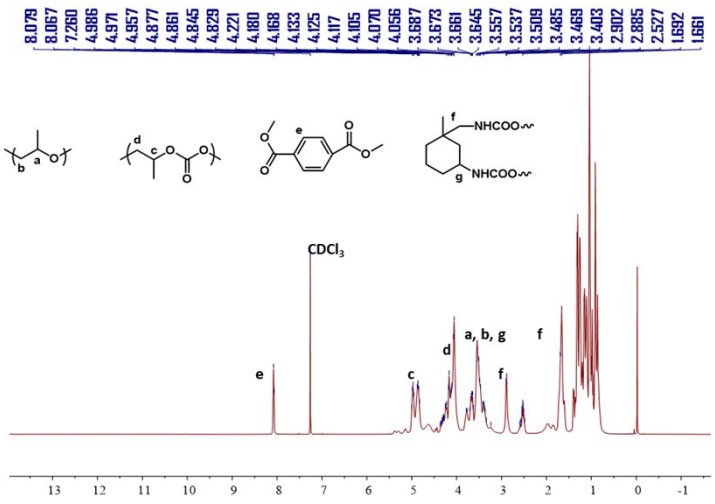


Fig. S22 [1]H-NMR spectrum of PPC-TDTD-4.

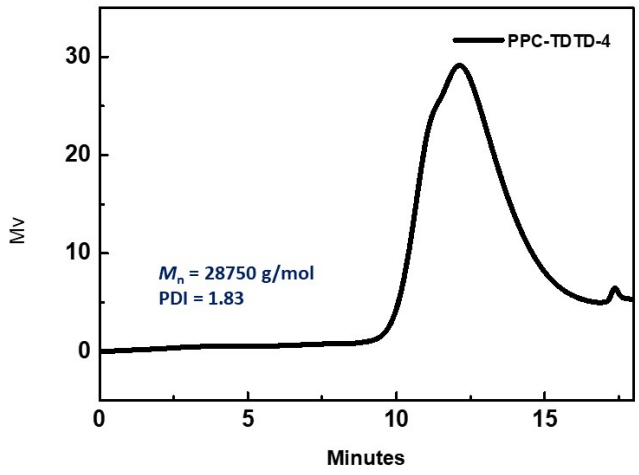


Fig. S23 GPC traces of PPC-TDTD-4.

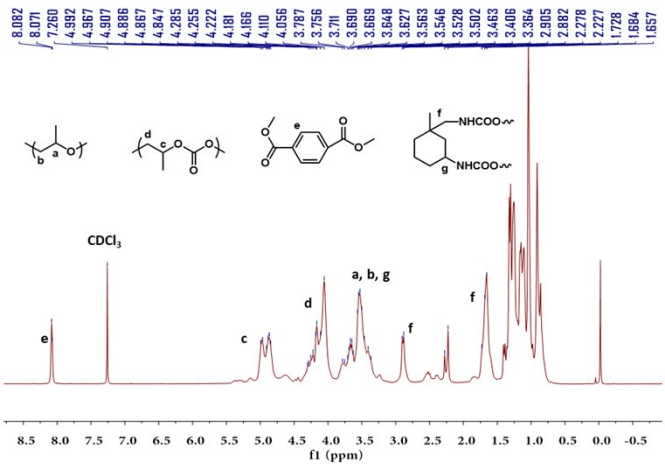


Fig. S24 [1]H-NMR spectrum of PPC-TDTD-4(1).

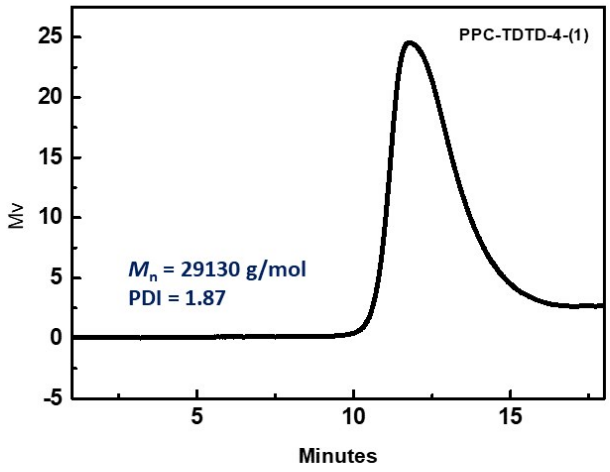


Fig. S25 GPC traces of PPC-TDTD-4(1).

$$\text{Content } (N^+, \%) = content\ of\ hydrophilic\ group\ (wt\ \%) \times \frac{M(N)}{M(CE)} \times \frac{n(HOAc)}{n}$$

M(N) means the sum of relative atomic mass of nitrogen in a molecule and M(CE) is the relative molecular mass of the corresponding chain extender, so the second term represents the mass fraction of nitrogen atoms; n(HOAc) refers to the actual molar amount of HOAc used in the preparation process and n is the theoretical molar amount of HOAc required under the assumption of 100% neutralization, therefore the third term represents the degree of neutralization.

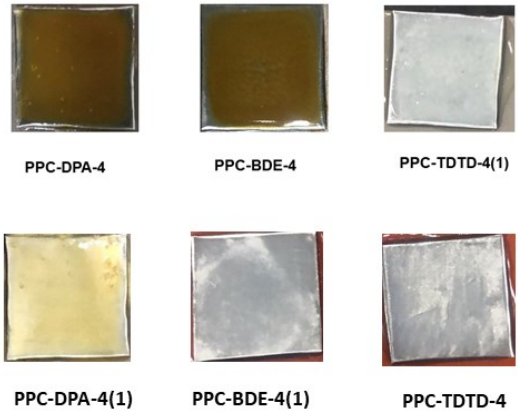


Fig. S26 The photographs of CS plates coated with PPC-DPA-4, PPC-DPA-4(1), PPC-BDE-4, PPC-BDE-4(1), PPC-TDTD-4 and PPC-TDTD-4(1).