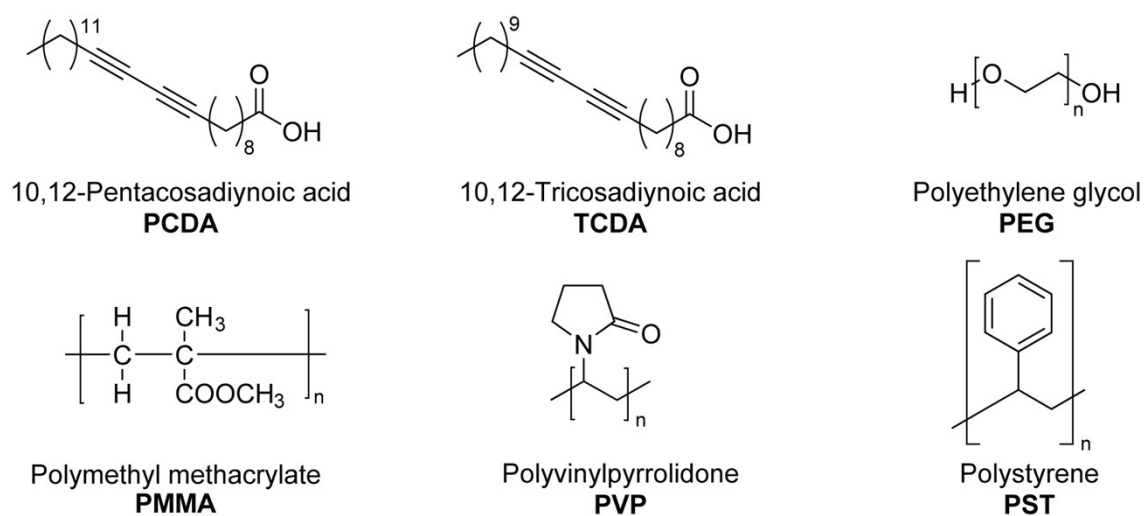# Supporting Information

Polydiacetylene/copolymer sensors to detect lung cancer breath volatile organic compounds
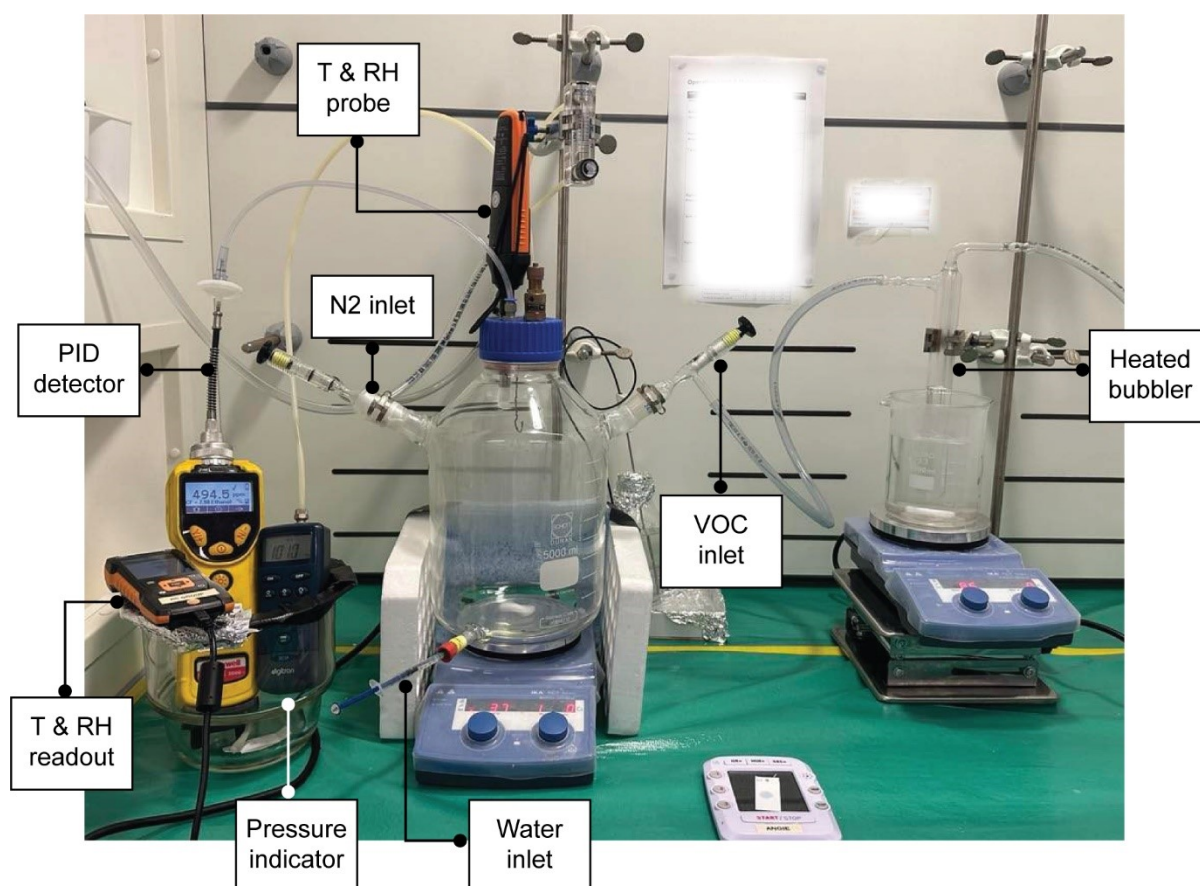
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Figure S1: Chemical structures of DA monomers and the copolymers investigated in this study.

10,12-Pentacosadiynoic acid
PCDA

10,12-Tricosadiynoic acid
TCDA

Polyethylene glycol
PEG

Polymethyl methacrylate
PMMA

Polyvinylpyrrolidone
PVP

Polystyrene
PST

Figure S2: Experimental setup for VOC sensitivity testing. Paper sensors are suspended in a pre-conditioned custom-built reactor. Temperature and RH are monitored using an in-built probe and controlled by adjusting the hotplate and injecting water through the bottom inlet. VOC dosing is done using a bubbler filled with the VOC solvent. Nitrogen gas is used as a carrier gas.
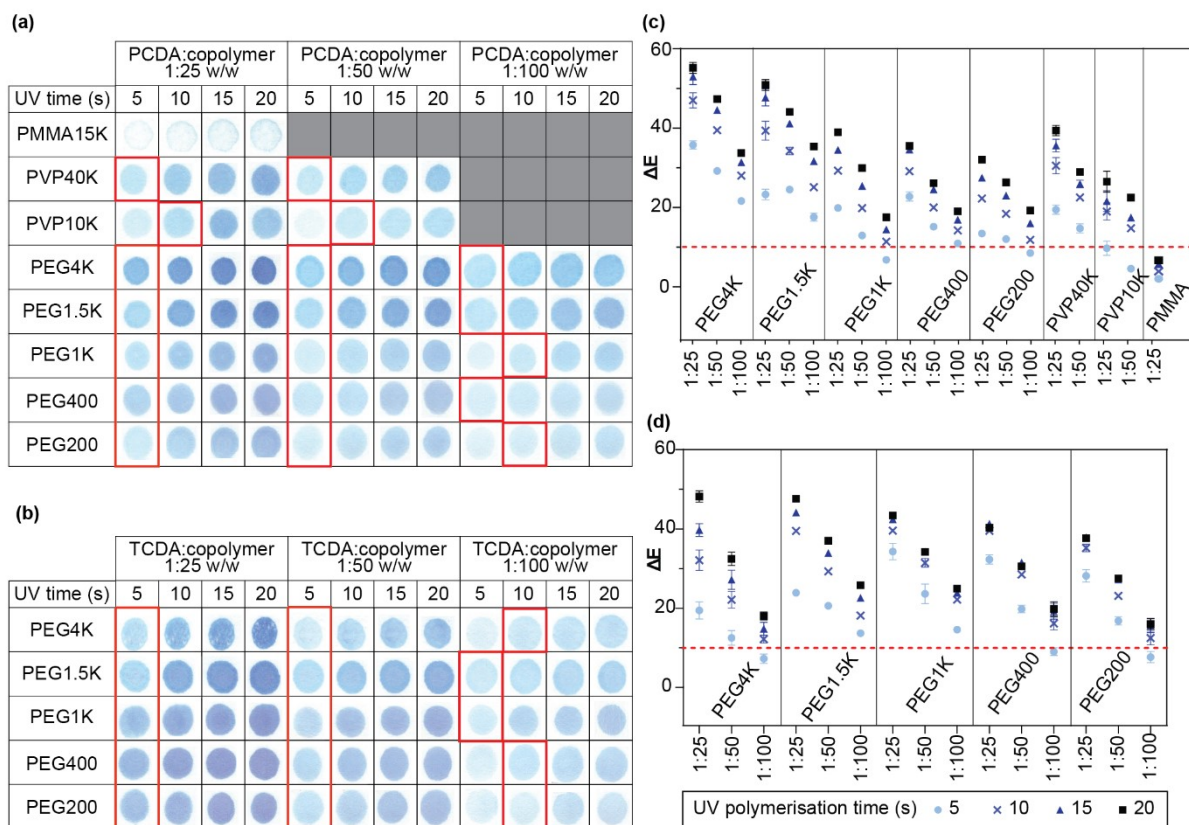
Figure S3: The blue intensity of (a) PCDA/copolymer and (b) TCDA/copolymer sensors with different weight ratios after 5 – 20 seconds of UV polymerization. The corresponding ΔE values are shown in c-d. The dashed magenta line at ΔE = 10 marks the value when color change can be seen via the naked eye. Grey boxes indicate no blue PDA was formed. PDA/PST was not formed in all formulations and hence, the whole row is excluded. The red border indicates the selected UV time. (n=3, error bars represent standard deviation).
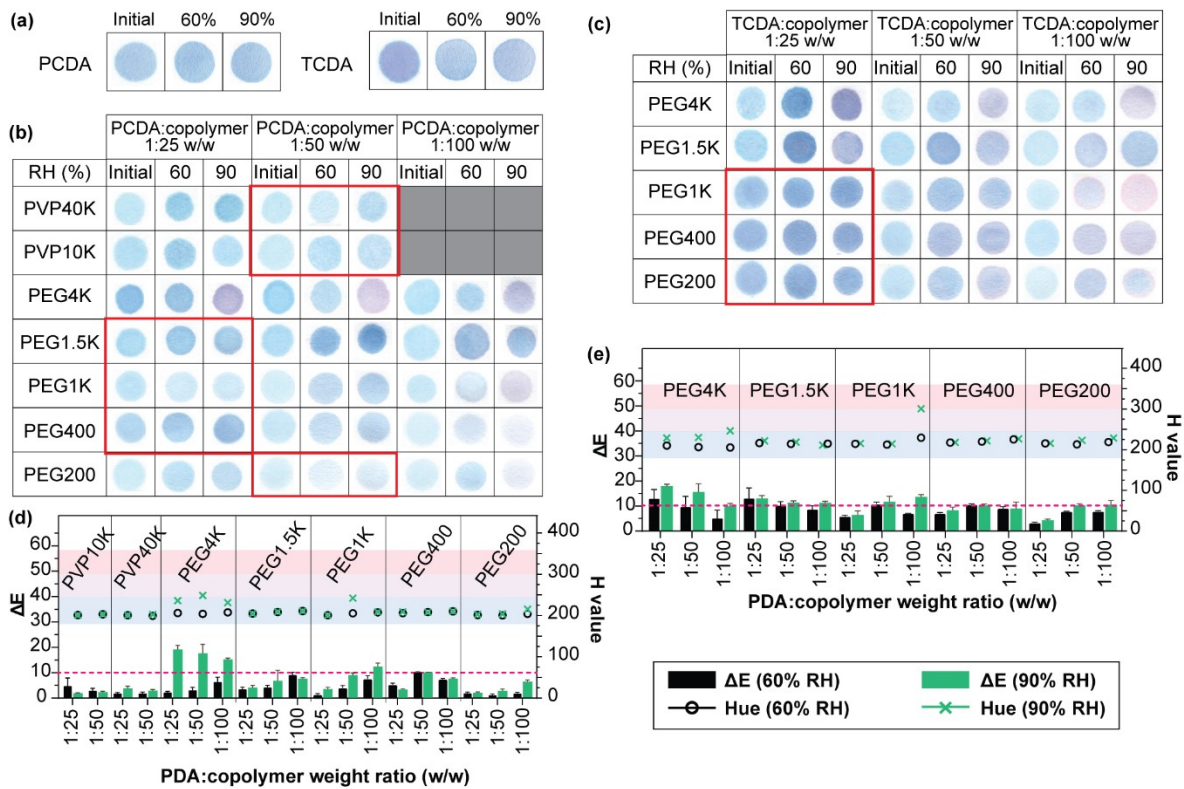
Figure S4: Colorimetric responses of (a) control PCDA and TCDA without copolymer, (b) PCDA/copolymer, and (c) TCDA/copolymer sensors after 30 minutes of exposure to standard breath temperature and relative humidity (35 °C and 60% RH or 90% RH), and (d-e) their ΔE and H values. The blue, purple and red sections highlight the H value where PDA is of that color. The dashed magenta line at ΔE = 10 marks the value when color change can be seen via the naked eye. Grey boxes indicate no blue PDA was formed. The red border indicates the selected formulation for further testing. (n=3, error bars represent standard deviation).

Table S1: Hildebrand solubility parameter (δhild), dispersion bond (δd), polar bond (δd), and hydrogen bond (δd) values (MPa$^{0.5}$) of the copolymers tested in this study and the VOCs.

Chemical	Type	δhild	δd	δp	δh
Undecane	VOC	14.6	16	0	0
Isoprene	VOC	15.1	14.8	2.8	5.6
Ethylbenzene	VOC	17.9	17.8	0.6	1.4
2-butanone	VOC	19.1	16	9	5.1
2-ethylhexanol	VOC	19.4	15.9	3.3	11.8
Acetone	VOC	20.3	15.5	10.4	7
Poly(ethylene glycol) (PEG)	Polymer	20.7	17	10.5	5.5
Polyvinylpyrrolidone (PVP)	Polymer	22.2	15.5	11.7	8.6
Hexanal	VOC	22.3	15.8	8.4	5.3
Poly(methyl methacrylate) (PMMA)	Polymer	22.7	18.6	10.5	7.5
Polystyrene (PST)	Polymer	23.9	22.8	5.8	4.3
Ethanol	VOC	26.0	15.8	8.8	19.4

Table S2: Hildebrand solubility parameter (δhild) differences (MPa$^{0.5}$) between the copolymers and the VOCs (difference = δhild copolymer – δhild VOC).

VOC	δhild difference	
	PEG	PVP
Undecane	6.1	7.6
Isoprene	5.6	7.1
Ethylbenzene	2.8	4.3
2-butanone	1.6	3.1
2-ethylhexanol	1.3	2.8
Acetone	0.4	1.9
Hexanal	-1.6	-0.1
Ethanol	-5.3	-3.8

Table S3: Selected lung cancer breath VOC biomarkers and their LC and healthy concentration range in the breath. Sensitivity (SST) is the ability to distinguish true positives in a population with disease. Specificity (SPC) is the ability to detect healthy subjects in a population without the disease of interest.

VOC	Patient range	Healthy range	SST (%)	SPC (%)	Ref
2-butanone	$1.78 - 8.38$ nmol/L[1] $3.8 - 38.8$ ppb[2]	$0.45 - 2.34$ nmol/L[1] $1.35 - 3.18$ ppb[3]	93	92.7	1-7
2-ethyl-1-hexanol	Unknown	Unknown	Unknown	98[8]	4,8,9
Ethylbenzene	$13.6 - 32.6 \times 10^{-12}$ M[10] $4.6 - 89.3$ ppb[2] $110 - 180$ ppb[11]	$10.8 - 15.1 \times 10^{-12}$ M[10]	100	81	2,10-12
Hexanal	$3.8 - 5.3$ ppb[2] $26.6 - 57.7$ ppb[13]	0 ppb[2] $7.0 - 13.8$ ppb[13]	100[14] 74[9]	71.7[14] 73[9] 100[2] 94[8]	2,4,12,13
Undecane	$20 - 28$ ppb[11] $0.08 - 4.50$ ppb[12]	Unknown	100[14] 80[7]	81[14]	4,11,12,14

Table S4: Qualitative representation of the change in ΔE values after VOC exposure at 60% RH and 90% RH when compared to its corresponding PDA control (i.e.: without copolymer). Reference signal is from Figure 2. Nominal categorization was done to better visualize the effect of copolymer addition on VOC response. (^) increase, (v) decrease, (-) insignificant or no change. VOCs abbreviation is 2-butanone (2BT), 2-ethylhexanol (2EH), ethylbenzene (EBZ), acetone (ACE), hexanal (HEX), undecane (UND), ethanol (ETH), and isoprene (IPR).

60% RH

VOC	PCDA						TCDA		
	PVP10K	PVP40K	PEG1.5K	PEG1K	PEG400	PEG200	PEG1K	PEG400	PEG200
2BT	^	^	^^	^	-	-	^^	^^	^^
2EH	^	^	^^	^	^	^	^^	^^	^^
EBZ	^	^	^^	^^	^	^	^^	^^	^^
ACE	^	-	^	^	v	-	^	v	v
HEX	^	^	^	^	^	v	^	v	^^
UND	^	^	^^	^	^	^	^^	^	^
ETH	^	^	^^	^	^	^	^^	^^	^^
IPR	-	^^	^	-	-	-	^^	^	^

90% RH

VOC	PCDA						TCDA		
	PVP10K	PVP40K	PEG1.5K	PEG1K	PEG400	PEG200	PEG1K	PEG400	PEG200
2BT	^	^	^^	^^	^^	-	^^	^^	^^
2EH	^	^^	^^	^	^	^	^^	^^	^^
EBZ	^	^	^^	^	^	^	^^	^^	^^
ACE	^	^	^^	^	^^	^	^^	^	^
HEX	vv	vv	vv	vv	vv	vv	^	v	^
UND	^	^	^^	^	^	^	^^	^	^
ETH	^	^	^^	^	^	^	^^	^^	^^
IPR	v	-	^	-	v	v	^	-	-

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