Supporting Information

Rationalizing the Formation of Porosity in Mechanochemically-Synthesized Polymers

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Inhalt

1. Materials

The monomers Naphthalene (NT) (Sigma Aldrich, 99% purity), Anthracene (AT) (TCI, >97% purity), Tetracene (TT) (TCI, >97% purity), Biphenyl (BP) (Acros Organics, 99% purity), *p*-Terphenyl (TP) (abcr, 99% purity), *p*-Quaterphenyl (QT) (abcr, 98% purity), 1,1,2,2-Tetraphenylethylene (TePE) (Sigma Aldrich, 98% purity), 1,1,4,4-Tetraphenyl-1,3-butadiene (TePB) (Acros Organics, 99% purity), Triphenylamine (TPA) (TCI, >98% purity), 2,4,6-Triphenyl-1,3,5-triazine (TPT) (TCI, >98% purity), 1,3,5-Triphenylbenzene (TPB) (Sigma Aldrich, 97% purity), 1,3,5-Tris(*p*-biphenyl)benzene (TBB) (TCI, >98% purity), Triphenylmethane (TPM) (Sigma Aldrich, 99% purity), Tetraphenylmethane (TePM) (BLD Pharm, 97% purity), Benzene (BZ) (TCI, >99.5% purity), and Hexaphenylbenzene (HPB) Sigma Aldrich, 98% purity), the liquid linkers 1,2-Dichloroethane (DCE) (Sigma Aldrich, 99.8% purity), 1,3-Dichloropropane (DCP) (Sigma Aldrich, 99% purity), 1,4-Dichlorobutane (DCB) (Sigma Aldrich, 99% purity), and Tetrachloromethane (CCl_4) (Sigma Aldrich, >99.9% purity), the solid linkers 1,4-Bis(chloromethyl)benzene (BCMB) (Sigma Aldrich, 98% purity), 1,3,5-Tris(bromomethyl)benzene (TBMB) (Sigma Aldrich, 97% purity), and 1,2,4,5-Tetrakis(bromomethyl)benzene (TeBMB) (Sigma Aldrich, 95% purity), and the Lewis acid Aluminium(III)chloride ($AlCl_3$) (anhydrous, Alfa Aesar, 98% purity) were purchased and used as received. The liquid linkers Dichloromethane (DCM) and Chloroform ($CHCl_3$) were purchased in p.A quality and placed over 4Å molecular sieves. All chemicals were stored and used under inert gas atmosphere.

2. Weights, Moles and Equivalents

Table S1. Overview over the weights, moles and equivalents used for the polymerization with various monomers (top) and various liquid and solid linkers (bottom).

Monomer	Abbreviation	Weight (g)	Moles (mmol)	Equivalents
Naphthalene	NT	0.209	1.63	1
Anthracene	AT	0.291	1.63	1
Tetracene	TT	0.372	1.63	1
Biphenyl	BP	0.252	1.63	1
***p*-Terphenyl**	TP	0.376	1.63	1
***p*-Quaterphenyl**	QP	0.500	1.63	1
Tetraphenylethylene	TePE	0.542	1.63	1
Tetraphenylbutadiene	TePB	0.585	1.63	1
Triphenylamine	TPA	0.400	1.63	1
Triphenyltriazine	TPT	0.505	1.63	1
Triphenylbenzene	TPB	0.500	1.63	1
Tris(*p*-biphenyl)benzene	TBB	0.872	1.63	1
Triphenylmethane	TPM	0.399	1.63	1
Tetraphenylmethane	TePM	0.523	1.63	1
Benzene	BZ	0.127	1.63	1
Hexaphenylbenzene	HPB	0.872	1.63	1

Linker	Abbreviation	Weight (g)	Moles (mmol)	Equivalents
Dichloromethane	DCM	0.831	9.79	6
Dichloroethane	DCE	0.969	9.79	6
Dichloropropane	DCP	1.110	9.79	6
Dichlorobutane	DCB	1.240	9.79	6
Bis(chloromethyl)benzene	BCMB	0.286	1.63	1
Chloroform	$CHCl_3$	1.170	9.79	6
Tris(bromomethyl)benzene	TBMB	0.582	1.63	1
Tetrachloromethane	CCl_4	1.510	9.79	6
Tetrakis(bromomethyl)benzene	TeBMB	0.734	1.63	1

3. Polymer Matrix Overview

Table S2. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical reaction of **Naphthalene, Anthracene** and **Tetracene** and various linkers. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
NT-DCM	Naphthalene	Dichloromethane	74	380	0.23
NT-DCE	Naphthalene	Dichloroethane	>99	57	0.05
NT-DCP	Naphthalene	Dichloropropane	65	8	0.02
NT-DCB	Naphthalene	Dichlorobutane	37	0	0.00
NT-BCMB	Naphthalene	Bis(chloromethyl)benzene	57	49	0.09
NT-$CHCl_3$	Naphthalene	Chloroform	55	762	0.43
NT-TBMB	Naphthalene	Tris(bromomethyl)benzene	>99	0	0.00
NT-CCl_4	Naphthalene	Tetrachloromethane	78	327	0.24
NT-TeBMB	Naphthalene	Tetrakis(bromomethyl)benzene	99	253	0.20
AT-DCM	Anthracene	Dichloromethane	54	101	0.23
AT-DCE	Anthracene	Dichloroethane	25	32	0.07
AT-DCP	Anthracene	Dichloropropane	11	6	0.01
AT-DCB	Anthracene	Dichlorobutane	0	0	0.00
AT-BCMB	Anthracene	Bis(chloromethyl)benzene	39	77	0.13
AT-$CHCl_3$	Anthracene	Chloroform	87	622	0.34
AT-TBMB	Anthracene	Tris(bromomethyl)benzene	>99	37	0.09
AT-CCl_4	Anthracene	Tetrachloromethane	45	306	-
AT-TeBMB	Anthracene	Tetrakis(bromomethyl)benzene	90	25	0.02
TT-DCM	Tetracene	Dichloromethane	>99	663	0.44
TT-DCE	Tetracene	Dichloroethane	>99	305	-
TT-DCP	Tetracene	Dichloropropane	80	174	0.22
TT-DCB	Tetracene	Dichlorobutane	14	31	0.09
TT-BCMB	Tetracene	Bis(chloromethyl)benzene	87	30	0.07
TT-$CHCl_3$	Tetracene	Chloroform	91	813	0.56
TT-TBMB	Tetracene	Tris(bromomethyl)benzene	56	44	0.13
TT-CCl_4	Tetracene	Tetrachloromethane	85	107	0.11
TT-TeBMB	Tetracene	Tetrakis(bromomethyl)benzene	98	6	0.01

Table S3. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical reaction of **Biphenyl, *p*-Terphenyl** and ***p*-Quaterphenyl** and various linkers. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
BP-DCM	Biphenyl	Dichloromethane	67	335	0.27
BP-DCE	Biphenyl	Dichloroethane	79	30	0.02
BP-DCP	Biphenyl	Dichloropropane	45	19	0.03
BP-DCB	Biphenyl	Dichlorobutane	0	0	0.00
BP-BCMB	Biphenyl	Bis(chloromethyl)benzene	12	39	0.09
BP-$CHCl_3$	Biphenyl	Chloroform	89	804	0.43
BP-TBMB	Biphenyl	Tris(bromomethyl)benzene	36	7	0.10
BP-CCl_4	Biphenyl	Tetrachloromethane	91	304	0.25
BP-TeBMB	Biphenyl	Tetrakis(bromomethyl)benzene	71	10	0.02
TP-DCM	*p*-Terphenyl	Dichloromethane	79	796	0.53
TP-DCE	*p*-Terphenyl	Dichloroethane	86	393	0.28
TP-DCP	*p*-Terphenyl	Dichloropropane	49	72	0.15
TP-DCB	*p*-Terphenyl	Dichlorobutane	26	0	0.00
TP-BCMB	*p*-Terphenyl	Bis(chloromethyl)benzene	46	5	0.01
TP-$CHCl_3$	*p*-Terphenyl	Chloroform	>99	935	0.53
TP-TBMB	*p*-Terphenyl	Tris(bromomethyl)benzene	53	15	0.03
TP-CCl_4	*p*-Terphenyl	Tetrachloromethane	>99	592	0.35
TP-TeBMB	*p*-Terphenyl	Tetrakis(bromomethyl)benzene	67	40	0.14
QP-DCM	*p*-Quaterphenyl	Dichloromethane	>99	493	0.28
QP-DCE	*p*-Quaterphenyl	Dichloroethane	>99	367	0.26
QP-DCP	*p*-Quaterphenyl	Dichloropropane	59	23	0.06
QP-DCB	*p*-Quaterphenyl	Dichlorobutane	35	0	0.00
QP-BCMB	*p*-Quaterphenyl	Bis(chloromethyl)benzene	35	21	0.04
QP-$CHCl_3$	*p*-Quaterphenyl	Chloroform	>99	878	0.52
QP-TBMB	*p*-Quaterphenyl	Tris(bromomethyl)benzene	62	51	0.14
QP-CCl_4	*p*-Quaterphenyl	Tetrachloromethane	>99	600	0.34
QP-TeBMB	*p*-Quaterphenyl	Tetrakis(bromomethyl)benzene	73	62	0.19

Table S4. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical reaction of **Tetraphenylethylene** and **Tetraphenylbutadiene** and various linkers. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
TePE-DCM	Tetraphenylethylene	Dichloromethane	97	261	0.20
TePE-DCE	Tetraphenylethylene	Dichloroethane	>99	105	0.13
TePE-DCP	Tetraphenylethylene	Dichloropropane	66	0	0.00
TePE-DCB	Tetraphenylethylene	Dichlorobutane	32	0	0.00
TePE-BCMB	Tetraphenylethylene	Bis(chloromethyl)benzene	36	21	0.04
TePE-$CHCl_3$	Tetraphenylethylene	Chloroform	>99	940	0.51
TePE-TBMB	Tetraphenylethylene	Tris(bromomethyl)benzene	50	22	0.05
TePE-CCl_4	Tetraphenylethylene	Tetrachloromethane	>99	370	-
TePE-TeBMB	Tetraphenylethylene	Tetrakis(bromomethyl)benzene	66	61	0.14
TePB-DCM	Tetraphenylbutadiene	Dichloromethane	>99	38	0.08
TePB-DCE	Tetraphenylbutadiene	Dichloroethane	96	19	0.03
TePB-DCP	Tetraphenylbutadiene	Dichloropropane	56	28	0.09
TePB-DCB	Tetraphenylbutadiene	Dichlorobutane	12	0	0.00
TePB-BCMB	Tetraphenylbutadiene	Bis(chloromethyl)benzene	42	0	0.00
TePB-$CHCl_3$	Tetraphenylbutadiene	Chloroform	94	429	0.28
TePB-TBMB	Tetraphenylbutadiene	Tris(bromomethyl)benzene	40	11	0.02
TePB-CCl_4	Tetraphenylbutadiene	Tetrachloromethane	>99	51	0.05
TePB-TeBMB	Tetraphenylbutadiene	Tetrakis(bromomethyl)benzene	53	13	0.03

Table S5. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical reaction of **Triphenylamine** and **Triphenyltriazine** and various linkers. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
TPA-DCM	Triphenylamine	Dichloromethane	34	54	0.10
TPA-DCE	Triphenylamine	Dichloroethane	10	6	0.01
TPA-DCP	Triphenylamine	Dichloropropane	43	7	0.01
TPA-DCB	Triphenylamine	Dichlorobutane	9	0	0.00
TPA-BCMB	Triphenylamine	Bis(chloromethyl)benzene	40	54	0.09
TPA-$CHCl_3$	Triphenylamine	Chloroform	>99	165	0.11
TPA-TBMB	Triphenylamine	Tris(bromomethyl)benzene	46	0	0.00
TPA-CCl_4	Triphenylamine	Tetrachloromethane	68	14	0.02
TPA-TeBMB	Triphenylamine	Tetrakis(bromomethyl)benzene	>99	0	0.00
TPT-DCM	Triphenyltriazine	Dichloromethane	55	18	0.05
TPT-DCE	Triphenyltriazine	Dichloroethane	33	29	0.12
TPT-DCP	Triphenyltriazine	Dichloropropane	25	16	0.03
TPT-DCB	Triphenyltriazine	Dichlorobutane	27	0	0.00
TPT-BCMB	Triphenyltriazine	Bis(chloromethyl)benzene	71	18	0.04
TPT-$CHCl_3$	Triphenyltriazine	Chloroform	86	47	0.09
TPT-TBMB	Triphenyltriazine	Tris(bromomethyl)benzene	90	22	0.05
TPT-CCl_4	Triphenyltriazine	Tetrachloromethane	45	13	0.02
TPT-TeBMB	Triphenyltriazine	Tetrakis(bromomethyl)benzene	83	15	0.04

Table S6. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical reaction of **Triphenylbenzene** and **Tris(*p*-biphenyl)benzene** and various linkers. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
TPB-DCM	Triphenylbenzene	Dichloromethane	95	1220	0.76
TPB-DCE	Triphenylbenzene	Dichloroethane	89	704	0.32
TPB-DCP	Triphenylbenzene	Dichloropropane	>99	34	0.05
TPB-DCB	Triphenylbenzene	Dichlorobutane	10	0	0.00
TPB-BCMB	Triphenylbenzene	Bis(chloromethyl)benzene	28	59	0.14
TPB-$CHCl_3$	Triphenylbenzene	Chloroform	>99	1310	0.68
TPB-TBMB	Triphenylbenzene	Tris(bromomethyl)benzene	45	492	0.31
TPB-CCl_4	Triphenylbenzene	Tetrachloromethane	>99	440	0.27
TPB-TeBMB	Triphenylbenzene	Tetrakis(bromomethyl)benzene	>99	23	0.06
TBB-DCM	Tris(*p*-biphenyl)benzene	Dichloromethane	84	1153	0.65
TBB-DCE	Tris(*p*-biphenyl)benzene	Dichloroethane	>99	341	0.22
TBB-DCP	Tris(*p*-biphenyl)benzene	Dichloropropane	>99	129	0.18
TBB-DCB	Tris(*p*-biphenyl)benzene	Dichlorobutane	41	7	0.01
TBB-BCMB	Tris(*p*-biphenyl)benzene	Bis(chloromethyl)benzene	37	0	0.11
TBB-$CHCl_3$	Tris(*p*-biphenyl)benzene	Chloroform	>99	1052	0.54
TBB-TBMB	Tris(*p*-biphenyl)benzene	Tris(bromomethyl)benzene	48	0	0.10
TBB-CCl_4	Tris(*p*-biphenyl)benzene	Tetrachloromethane	>99	650	0.36
TBB-TeBMB	Tris(*p*-biphenyl)benzene	Tetrakis(bromomethyl)benzene	70	222	0.33

Table S7. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical reaction of **Triphenylmethane** and **Tetraphenylmethane** and various linkers. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
TPM-DCM	Triphenylmethane	Dichloromethane	54	3	0.01
TPM-DCE	Triphenylmethane	Dichloroethane	>99	37	0.05
TPM-DCP	Triphenylmethane	Dichloropropane	22	0	0.00
TPM-DCB	Triphenylmethane	Dichlorobutane	0	0	0.00
TPM-BCMB	Triphenylmethane	Bis(chloromethyl)benzene	24	0	0.15
TPM-$CHCl_3$	Triphenylmethane	Chloroform	>99	33	0.07
TPM-TBMB	Triphenylmethane	Tris(bromomethyl)benzene	33	32	0.09
TPM-CCl_4	Triphenylmethane	Tetrachloromethane	0	0	0.00
TPM-TeBMB	Triphenylmethane	Tetrakis(bromomethyl)benzene	54	6	0.01
TePM-DCM	Tetraphenylmethane	Dichloromethane	19	16	0.05
TePM-DCE	Tetraphenylmethane	Dichloroethane	43	9	0.01
TePM-DCP	Tetraphenylmethane	Dichloropropane	1	0	0.00
TePM-DCB	Tetraphenylmethane	Dichlorobutane	0	0	0.00
TePM-BCMB	Tetraphenylmethane	Bis(chloromethyl)benzene	13	41	0.11
TePM-$CHCl_3$	Tetraphenylmethane	Chloroform	29	0	0.00
TePM-TBMB	Tetraphenylmethane	Tris(bromomethyl)benzene	31	7	0.03
TePM-CCl_4	Tetraphenylmethane	Tetrachloromethane	63	13	0.03
TePM-TeBMB	Tetraphenylmethane	Tetrakis(bromomethyl)benzene	43	21	0.04

Table S8. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical reaction of **Benzene** and **Hexaphenylbenzene** and various linkers. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
BZ-DCM	Benzene	Dichloromethane	23	14	0.02
BZ-DCE	Benzene	Dichloroethane	>99	39	0.07
BZ-DCP	Benzene	Dichloropropane	5	0	0.00
BZ-DCB	Benzene	Dichlorobutane	0	0	0.00
BZ-BCMB	Benzene	Bis(chloromethyl)benzene	13	0	0.00
BZ-$CHCl_3$	Benzene	Chloroform	42	353	0.22
BZ-TBMB	Benzene	Tris(bromomethyl)benzene	47	11	0.03
BZ-CCl_4	Benzene	Tetrachloromethane	0	0	0.00
BZ-TeBMB	Benzene	Tetrakis(bromomethyl)benzene	82	63	0.13
HPB-DCM	Hexaphenylbenzene	Dichloromethane	82	1069	0.67
HPB-DCE	Hexaphenylbenzene	Dichloroethane	>99	610	0.34
HPB-DCP	Hexaphenylbenzene	Dichloropropane	86	23	0.03
HPB-DCB	Hexaphenylbenzene	Dichlorobutane	37	54	0.19
HPB-BCMB	Hexaphenylbenzene	Bis(chloromethyl)benzene	89	87	0.22
HPB-$CHCl_3$	Hexaphenylbenzene	Chloroform	>99	875	0.46
HPB-TBMB	Hexaphenylbenzene	Tris(bromomethyl)benzene	85	72	0.16
HPB-CCl_4	Hexaphenylbenzene	Tetrachloromethane	>99	646	0.38
HPB-TeBMB	Hexaphenylbenzene	Tetrakis(bromomethyl)benzene	93	0	0.00

Table S9. Overview over the yield, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for porous polymers obtained during the mechanochemical **self-polymerization (SP) of solid linkers**. All reactions were proceeded at 30 Hz for 60 min in a MM500 mixer mill using ZrO_2 as milling material and $AlCl_3$ as Lewis acid and as bulking material.

Polymer	Monomer	Linker	Yield (%)	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
SP-BCMB	-	Bis(chloromethyl)benzene	90	86	0.14
SP-TBMB	-	Tris(bromomethyl)benzene	>99	706	0.42
SP-TeBMB	-	Tetrakis(bromomethyl)benzene	>99	207	0.22

4. Characterization

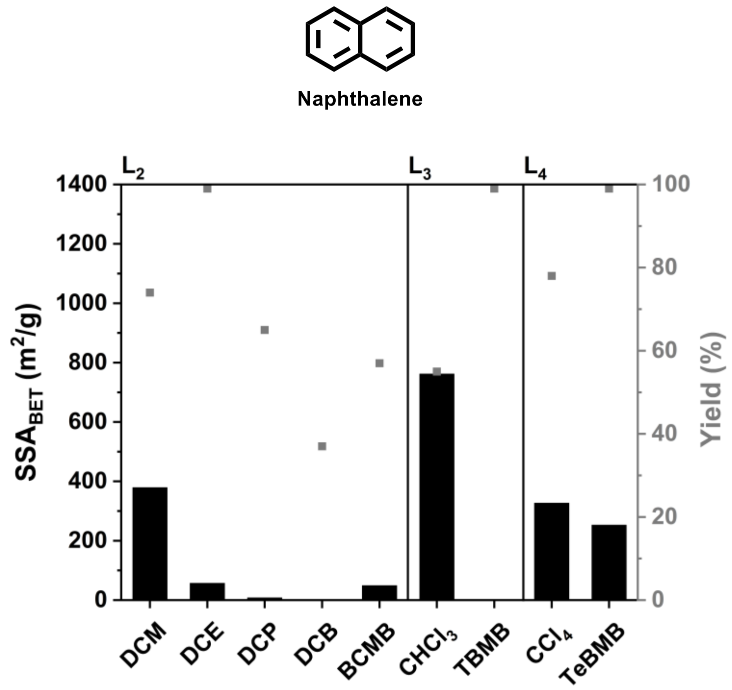


Figure S1. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Naphthalene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

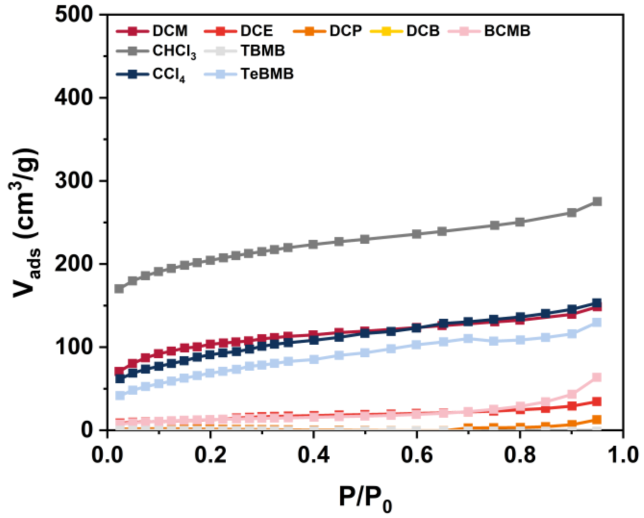


Figure S2. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Naphthalene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).

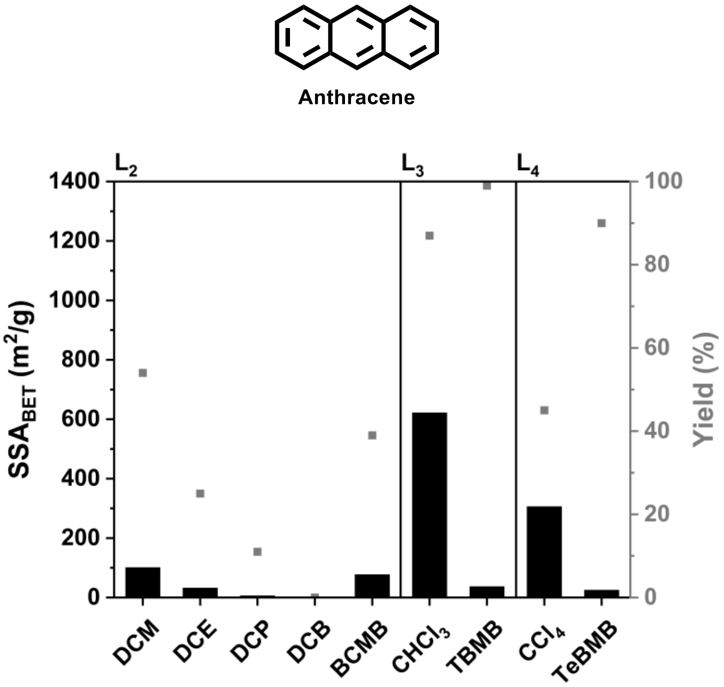


Figure S3. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Anthracene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

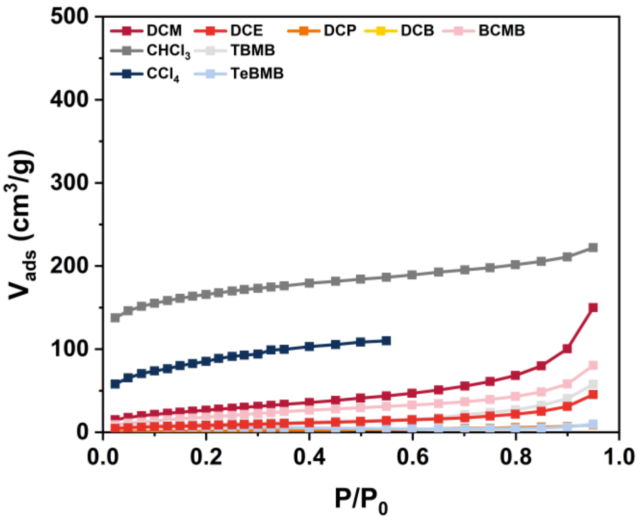


Figure S4. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Anthracene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).

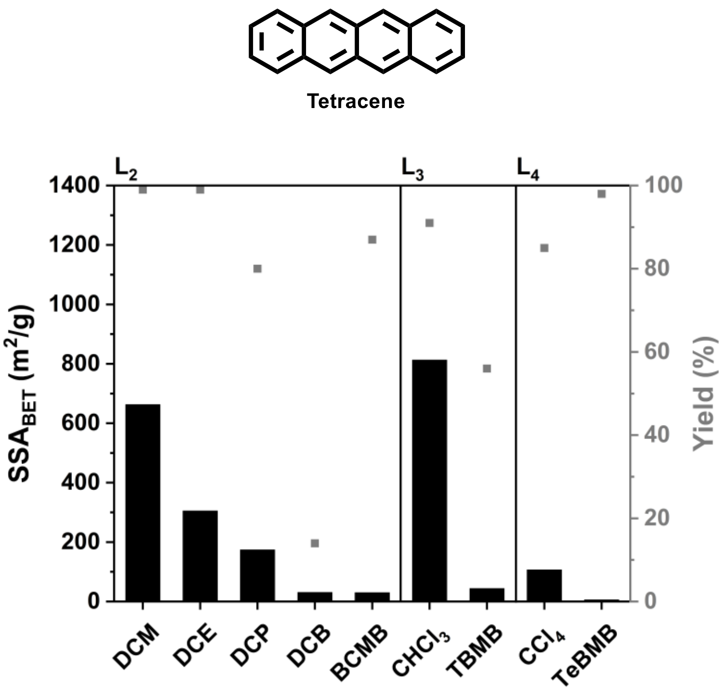


Figure S5. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Tetracene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

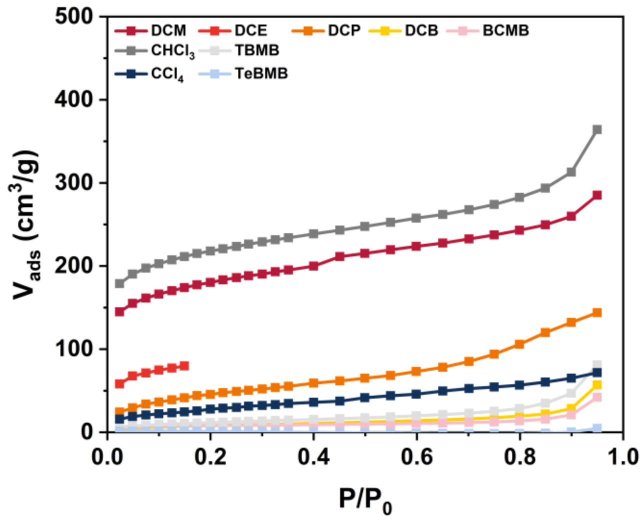


Figure S6. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Tetracene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).

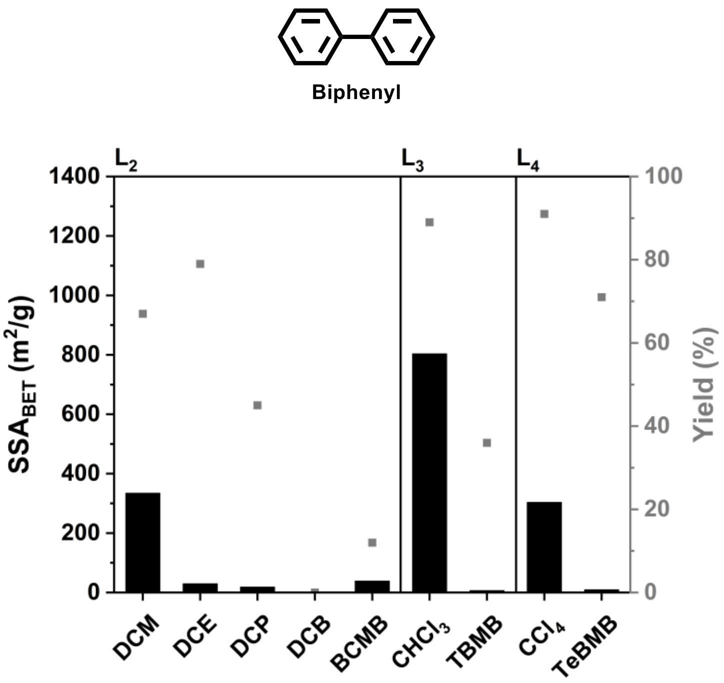


Figure S7. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Biphenyl and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

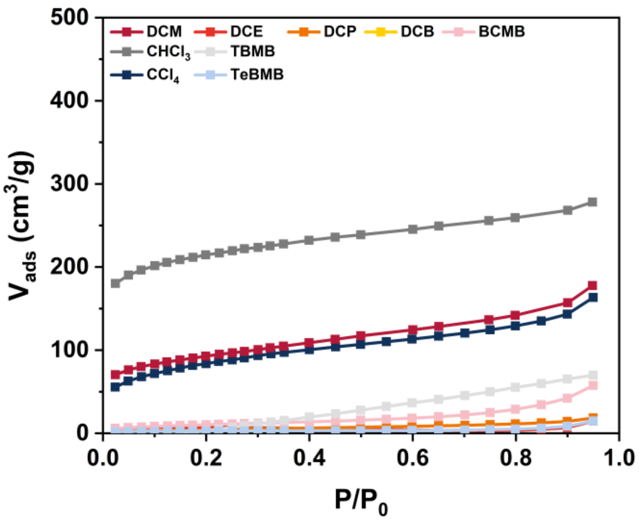


Figure S8. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Biphenyl as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).

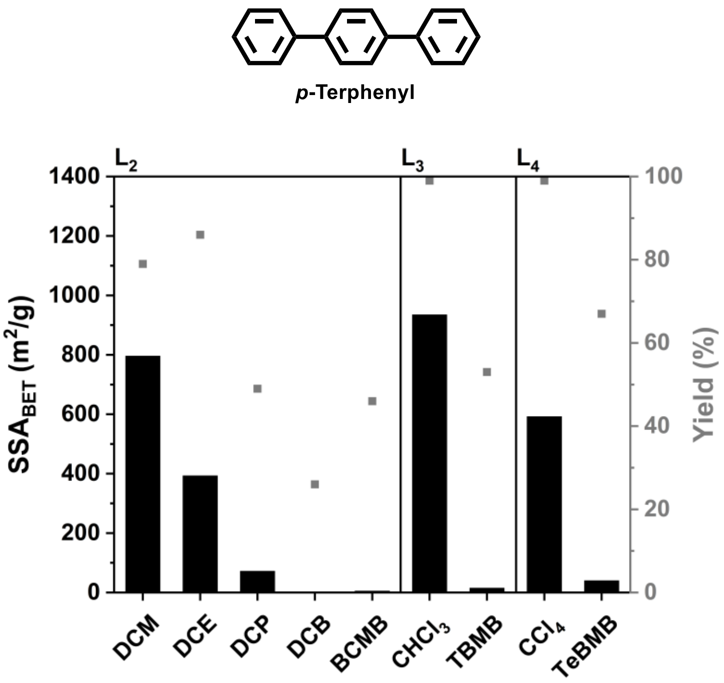


Figure S9. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer *p*-Terphenyl and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

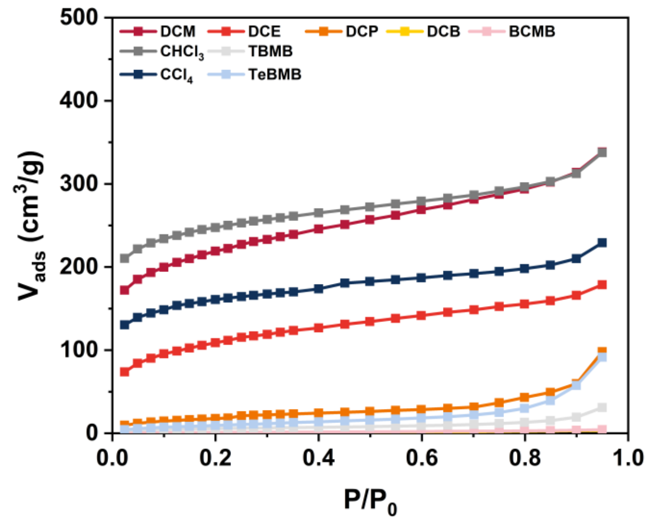
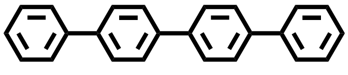


Figure S10. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with *p*-Terphenyl as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



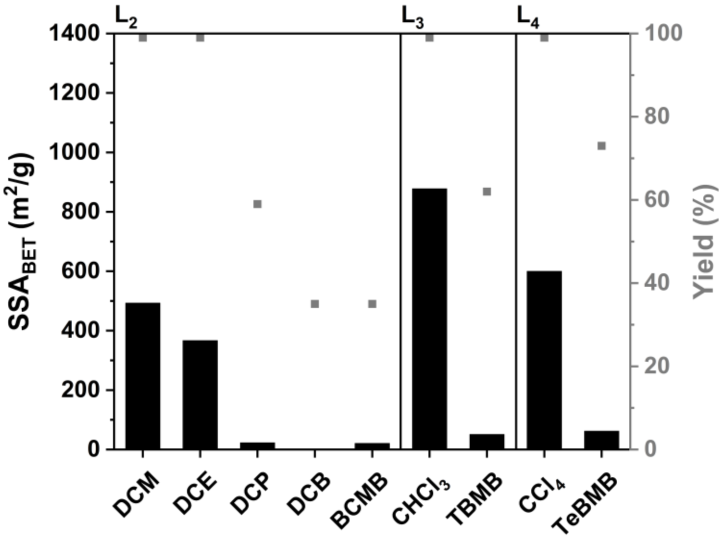


Figure S11. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer *p*-Quaterphenyl and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

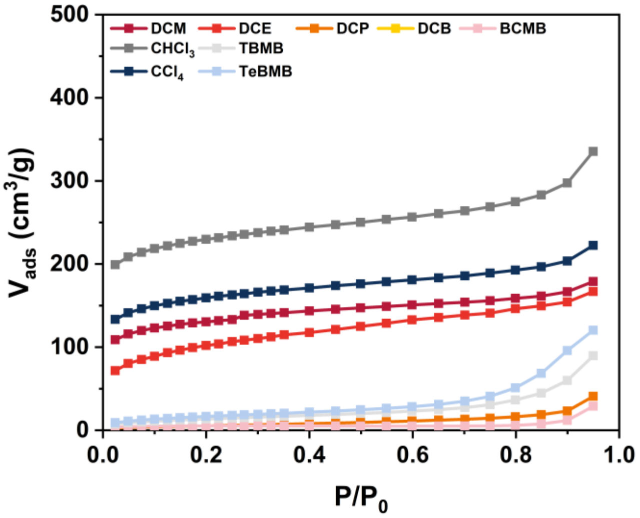
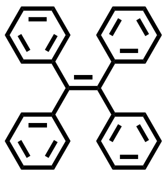


Figure S12. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with *p*-Quaterphenyl as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



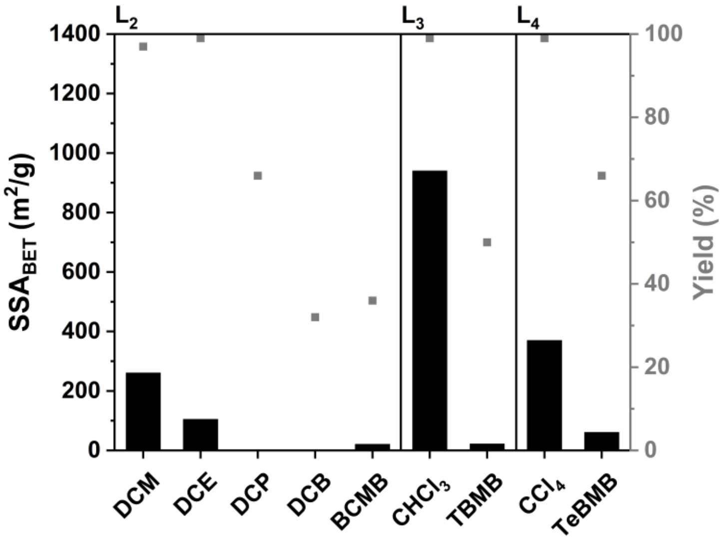


Figure S13. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Tetraphenylethylene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

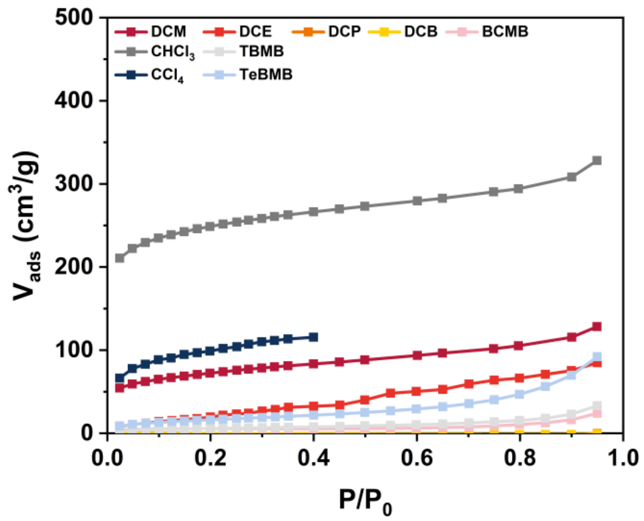
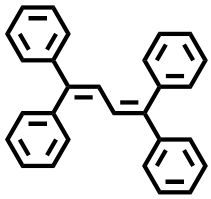


Figure S14. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Tetraphenylethylene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



Tetraphenylbutadiene

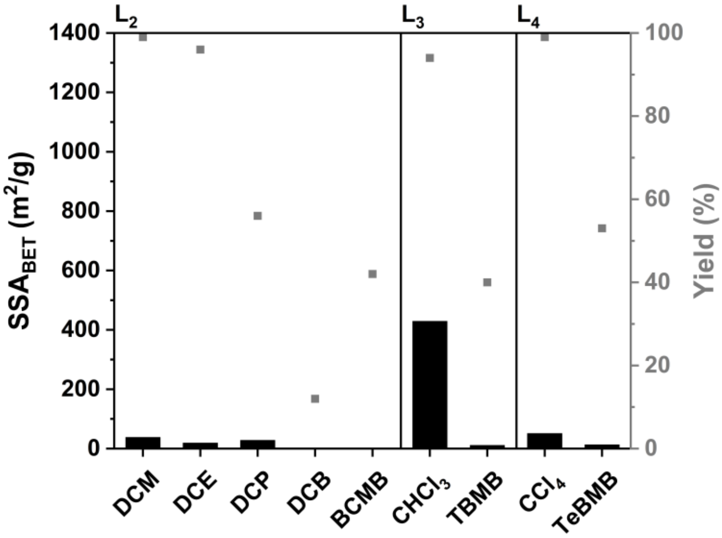


Figure S15. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Tetraphenylbutadiene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

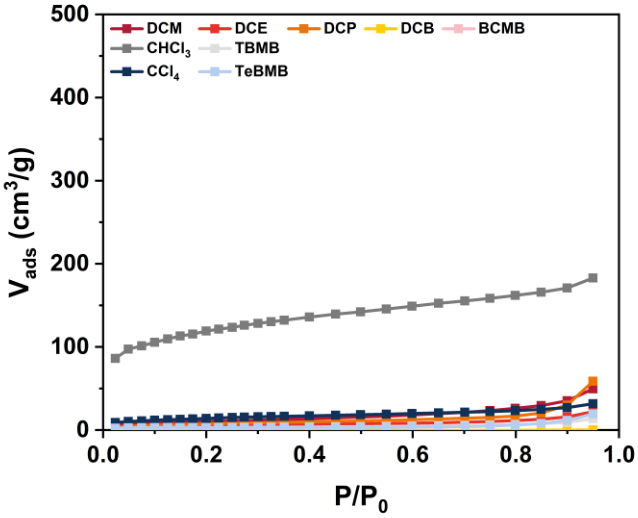


Figure S16. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Tetraphenylbutadiene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).

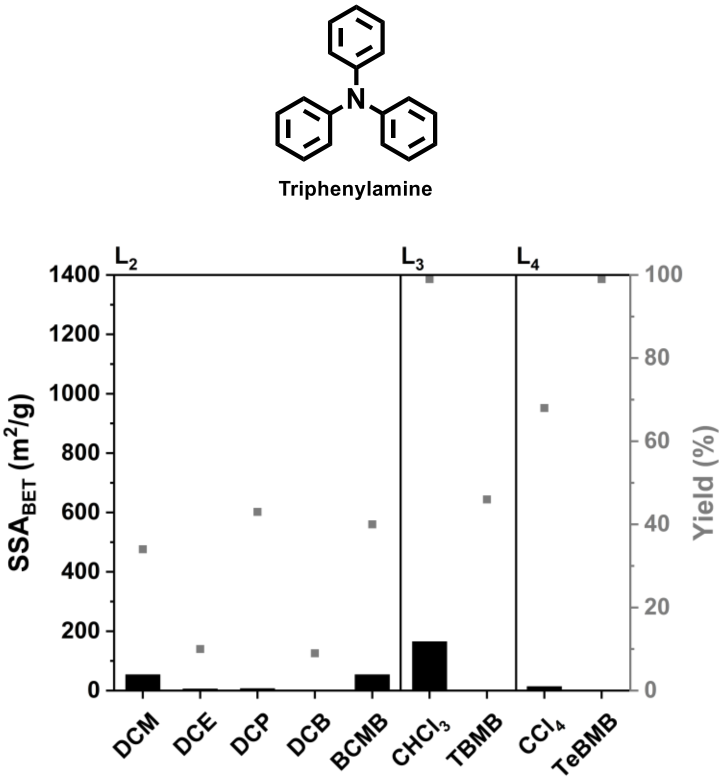


Figure S17. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Triphenylamine and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

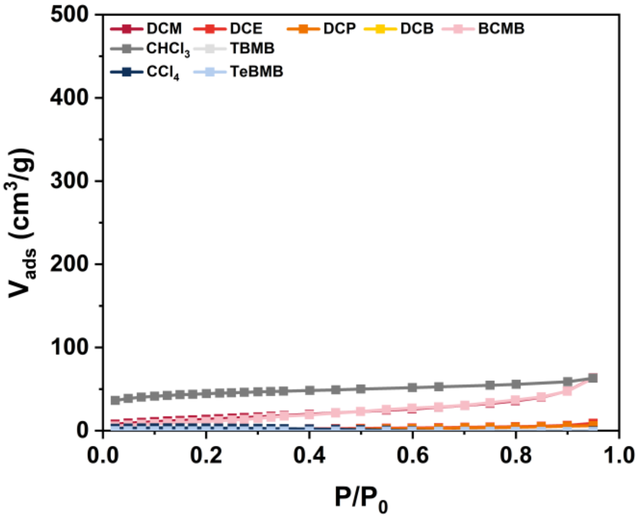
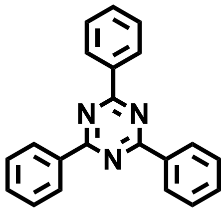


Figure S18. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Triphenylamine as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



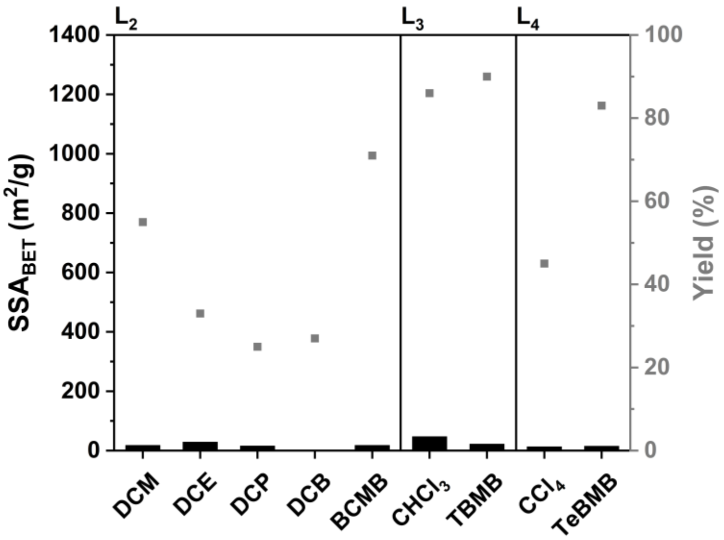


Figure S19. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Triphenyltriazine and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

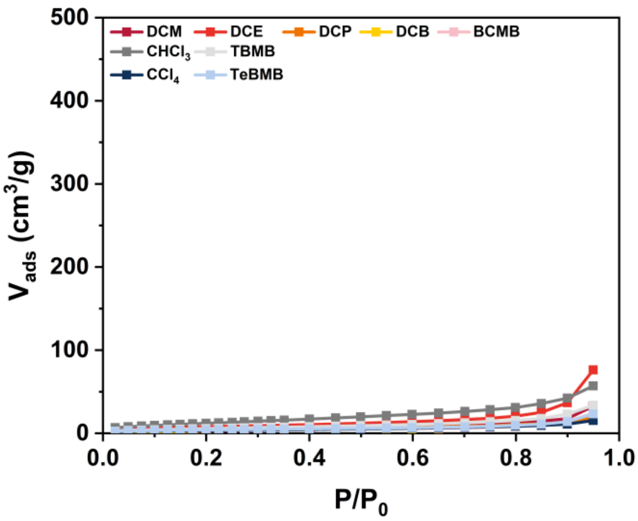
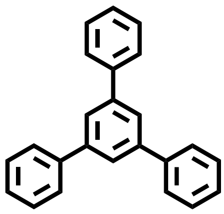


Figure S20. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Triphenyltriazine as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



Triphenylbenzene

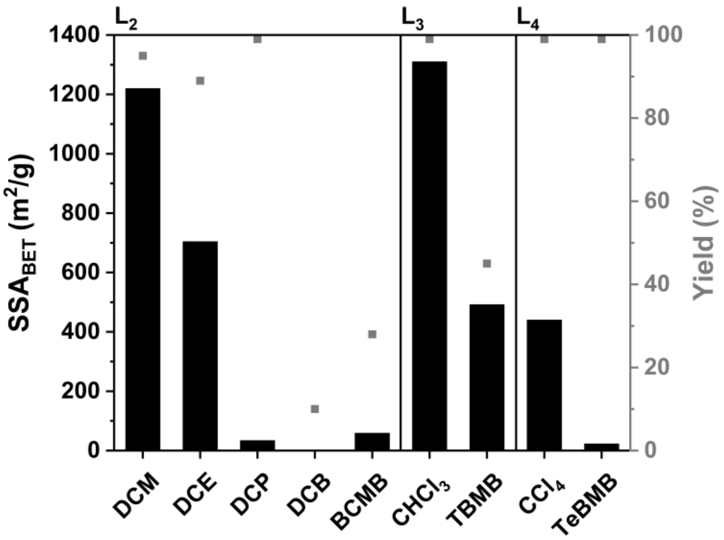


Figure S21. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Triphenylbenzene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

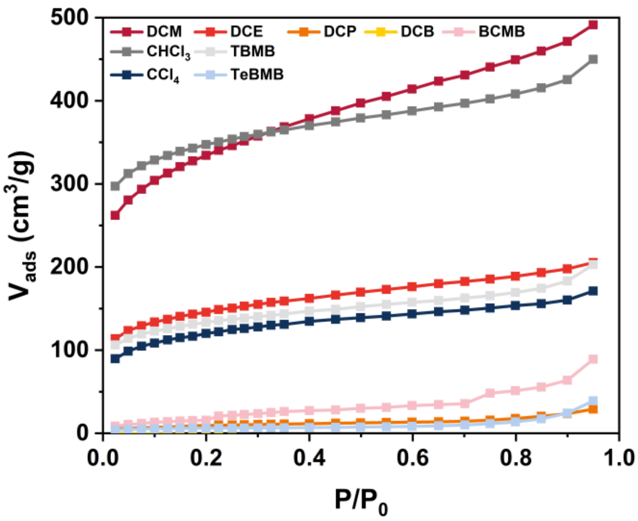
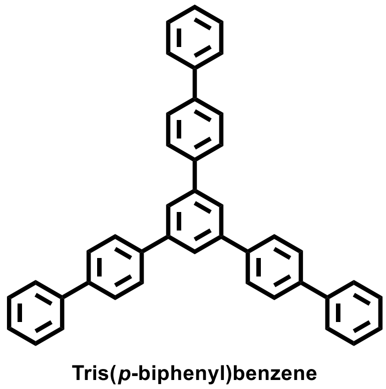


Figure S22. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Triphenylbenzene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



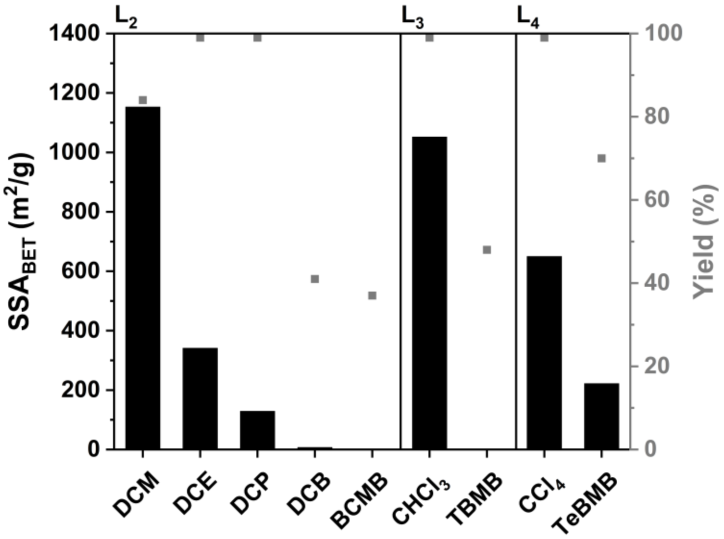


Figure S23. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Tris(*p*-biphenyl)benzene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

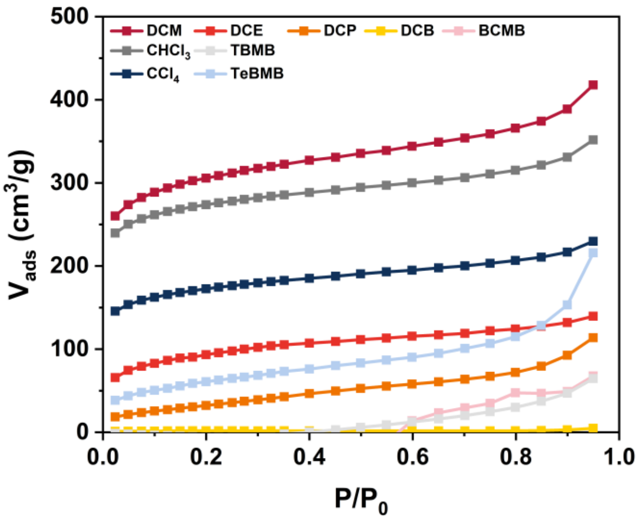
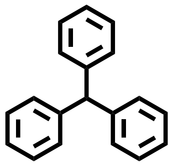


Figure S24. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Tris(*p*-biphenyl)benzene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



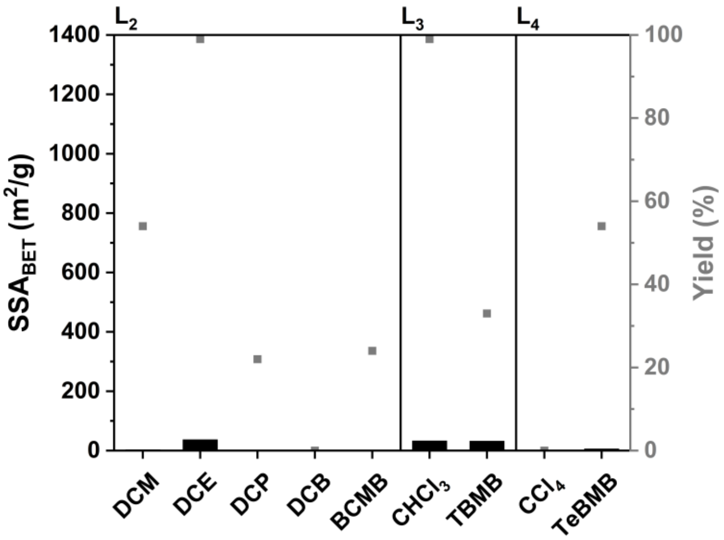


Figure S25. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Triphenylmethane and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

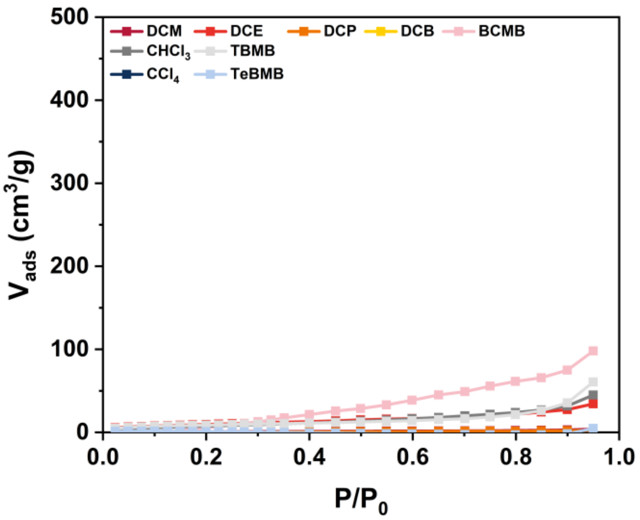
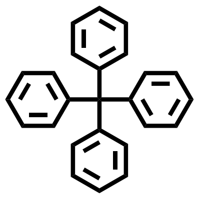


Figure S26. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Triphenylmethane as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



Tetraphenylmethane

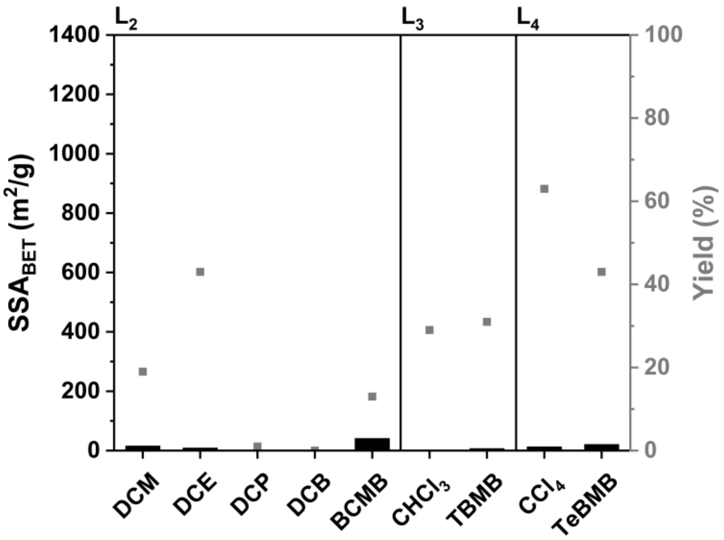


Figure S27. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Tetraphenylmethane and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

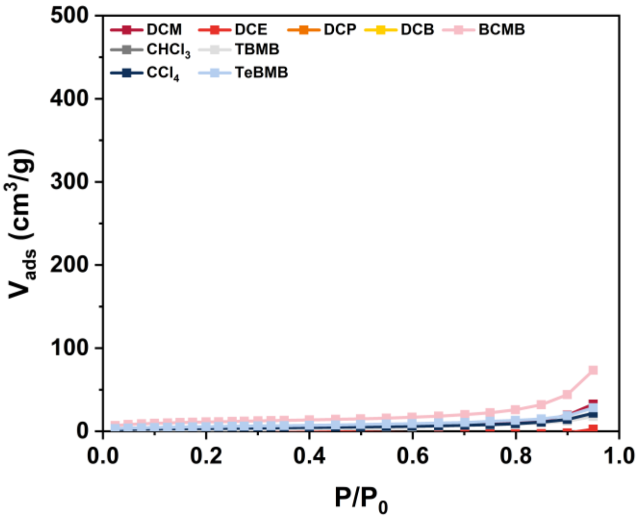


Figure S28. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Tetraphenylmethane as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).

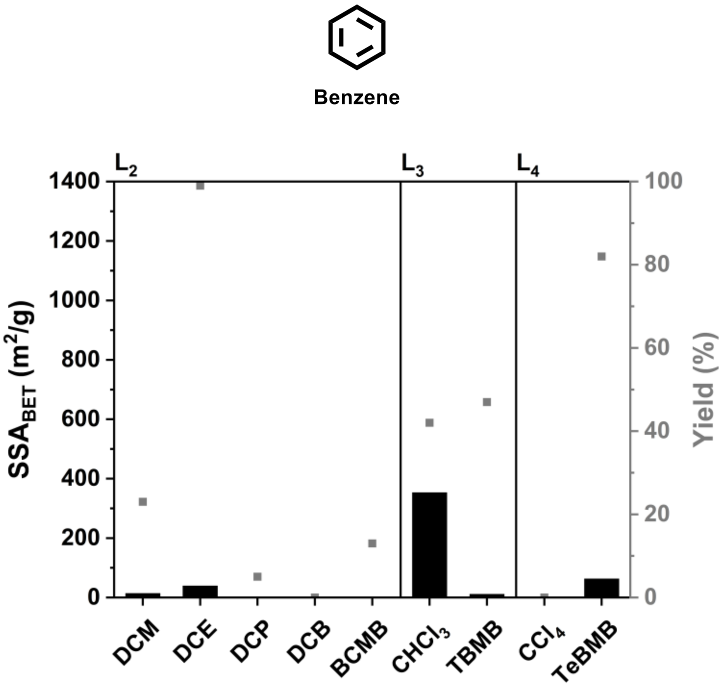


Figure S29. SSA$_{BET}$ (black bars) and yield (gray squares) for the polymerization of the monomer Benzene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

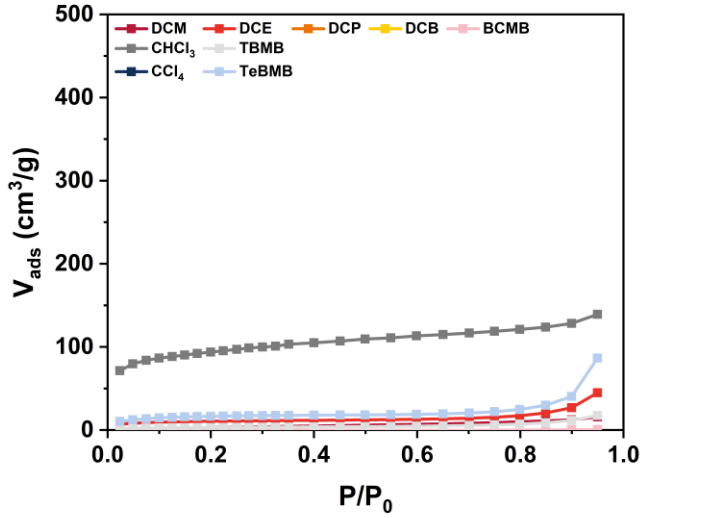
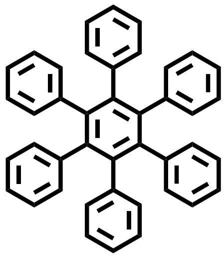


Figure S30. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Benzene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



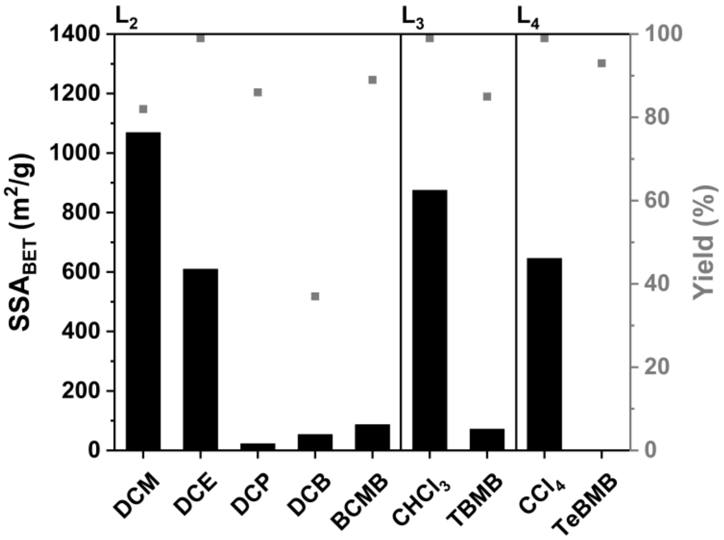


Figure S31. SSA_{BET} (black bars) and yield (gray squares) for the polymerization of the monomer Hexaphenylbenzene and various linkers. The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

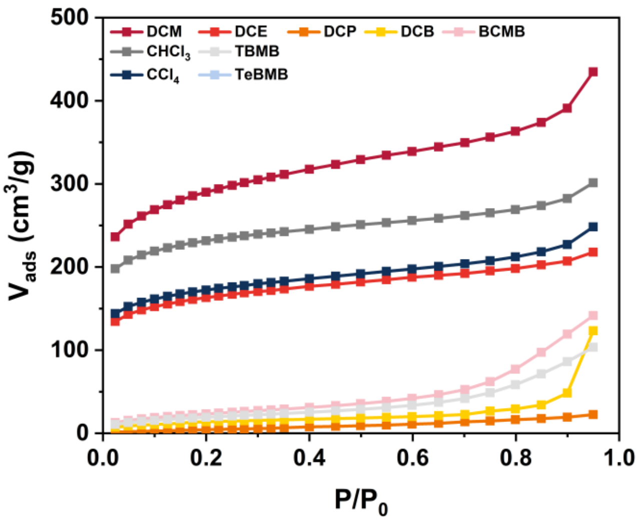
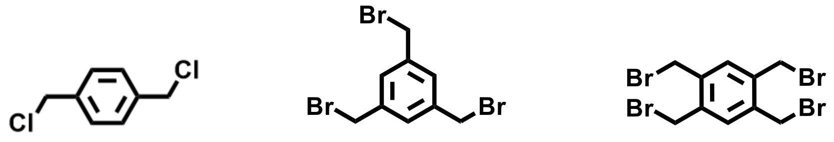


Figure S32. N_2 Physisorption measurements, showing the adsorption isotherms of polymers synthesized with Hexaphenylbenzene as monomer and various linkers. The linkers used are: Dichloromethane (DCM; dark red), Dichloroethane (DCE, light red), Dichloropropane (DCP, orange), Dichlorobutane (DCB, yellow), Bis(chloromethyl)benzene (BCMB, pink), Chloroform ($CHCl_3$, dark gray), Tris(bromomethyl)benzene (TBMB, light gray), Tetrachloromethane (CCl_4, dark blue), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).



Bis(chloromethyl)benzene **Tris(bromomethyl)benzene** **Tetrakis(bromomethyl)benzene**

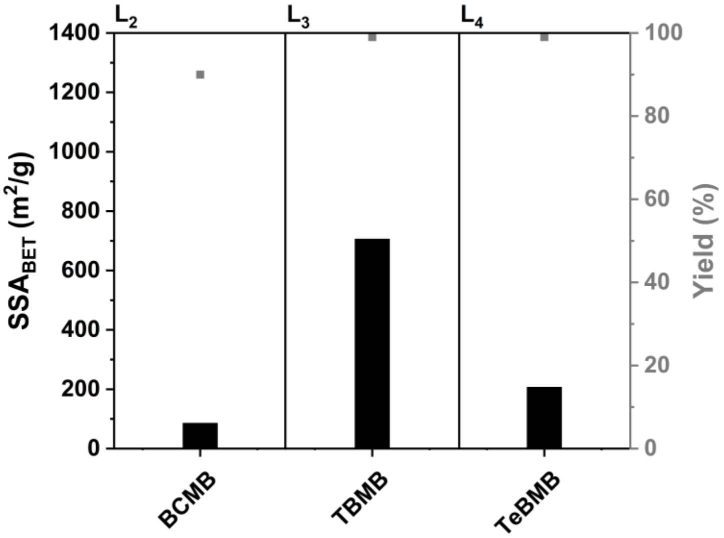


Figure S33. SSA_{BET} (black bars) and yield (gray squares) for the self-polymerization of the solid linkers Bis(chloromethyl)benzene (BCMB), Tris(bromomethyl)benzene (TBMB) and Tetrakis(bromomethyl)benzene (TeBMB). The linkers are divided into linkers with two linking points (L_2), three linking points (L_3) and four linking points (L_4).

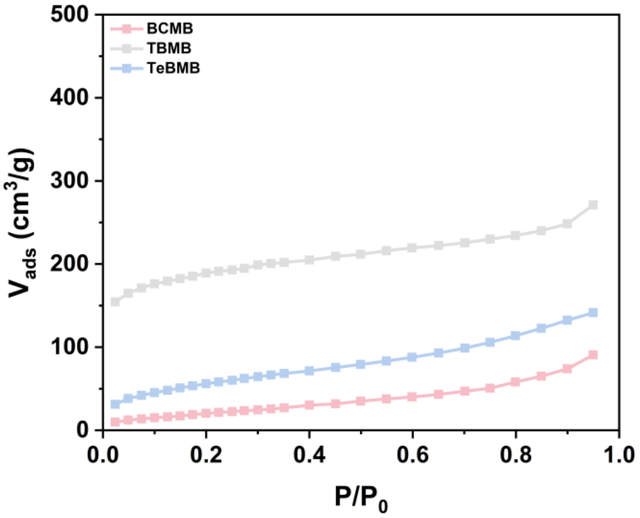


Figure S34. N_2 Physisorption measurements, showing the adsorption isotherms for the self-polymerization of the solid linkers. The linkers used are Bis(chloromethyl)benzene (BCMB, pink), Tris(bromomethyl)benzene (TBMB, light gray), and Tetrakis(bromomethyl)benzene (TeBMB, light blue).

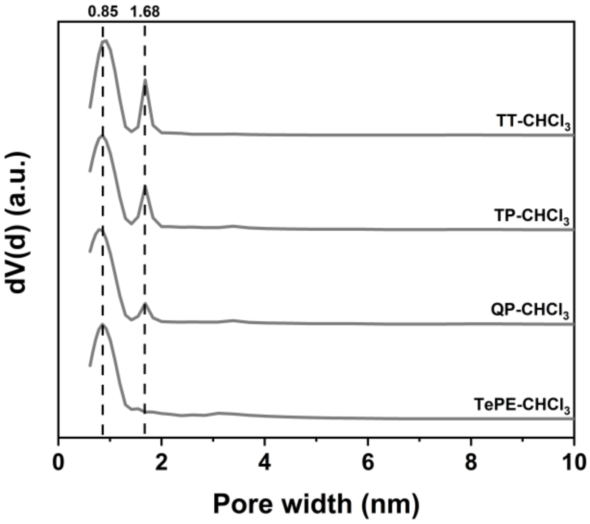


Figure S35. Pore size distributions for polymers featuring total pore volumes of >0.5 cm^3/g, obtained by polymerization of C_2 monomers. The polymers are comprising of a combination of the monomers Tetracene (TT), *p*-Terphenyl (TP), *p*-Quaterphenyl (QP) or Tetraphenylethene (TePE) and the linker Chloroform ($CHCl_3$, dark gray). As no kernel is available specifically for polymers, the pore size distributions were obtained by DFT calculation applying the calculation model N_2 at 77 K on carbon (slit pore, QSDFT equilibrium model), to take surface roughness and heterogeneity into account. The pore widths are shown in a range between 0 and 10 nm.

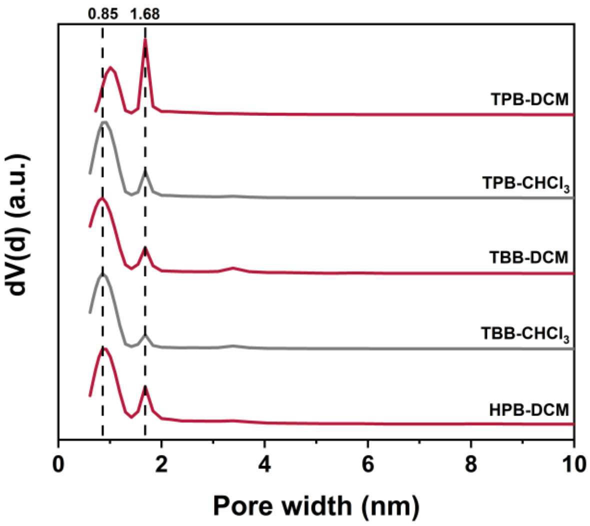


Figure S36. Pore size distributions for polymers featuring total pore volumes of >0.5 cm^3/g, obtained by polymerization of C_3 and C_6 monomers. The polymers are comprising of a combination of the monomers Triphenylbezene (TPB), Tris(*p*-biphenyl)benzene (TBB) or Hexaphenylbenzene (HPB) and the linkers Dichloromethane (DCM; dark red) or Chloroform ($CHCl_3$, dark gray). As no kernel is available specifically for polymers, the pore size distributions were obtained by DFT calculation applying the calculation model N_2 at 77 K on carbon (slit pore, QSDFT equilibrium model), to take surface roughness and heterogeneity into account. The pore widths are shown in a range between 0 and 10 nm.

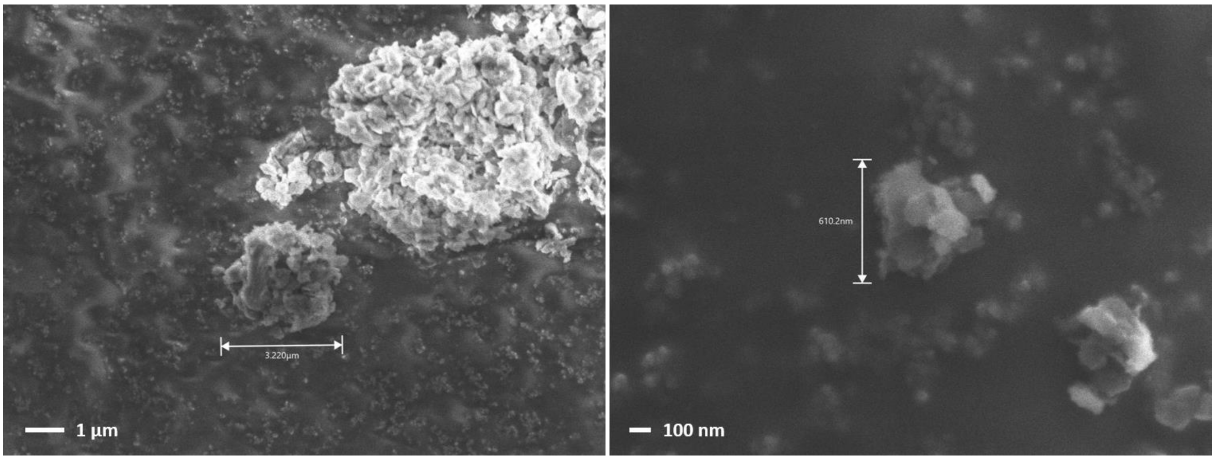


Figure S37. SEM image of the porous polymer TP-$CHCl_3$ in a magnification of 8 k (left) and of 43 k (right). Smaller particles are building broader agglomerates. The measured particle sizes are 3.220 µm (left) and 610.2 nm (right).

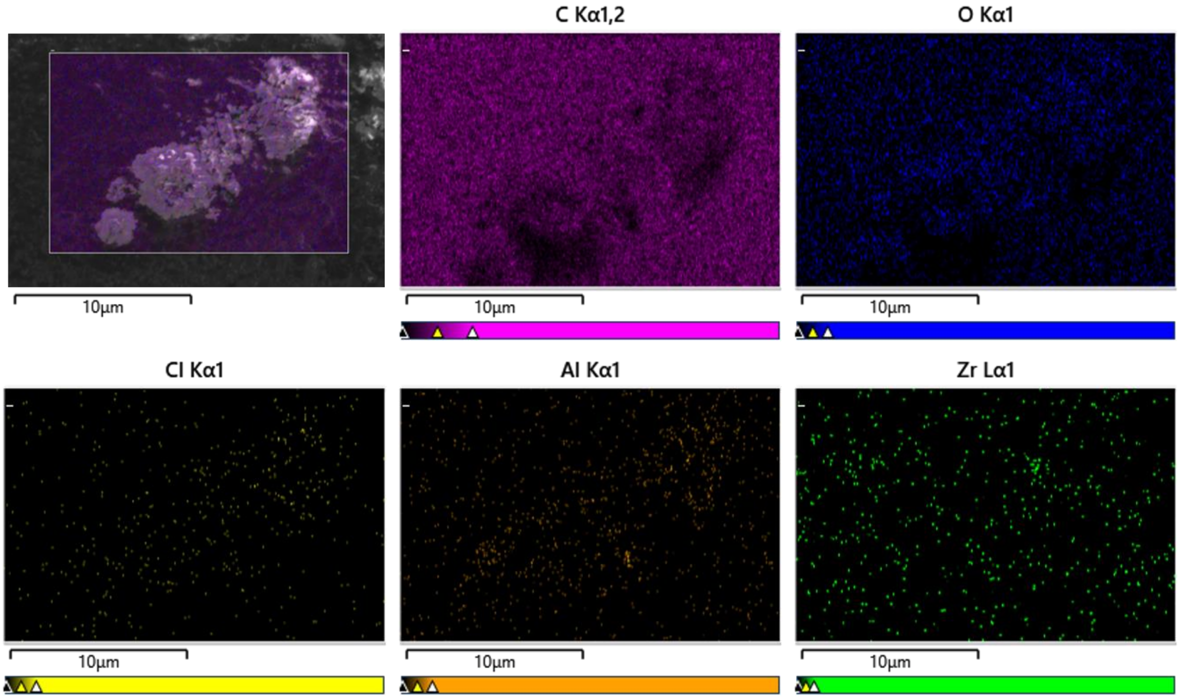


Figure S38. EDS analysis of the porous polymer TP-$CHCl_3$ showing the amount of carbon (purple), oxygen (blue), chlorine (yellow), aluminium (orange) and zirconium (green) in a specific particle.

Table S10. EDS analysis of TP-$CHCl_3$.

	C	O	Cl	Al	Zr
Mass %	93.55	5.25	0.85	0.35	0.00
Atom %	95.52	4.03	0.29	0.16	0.00

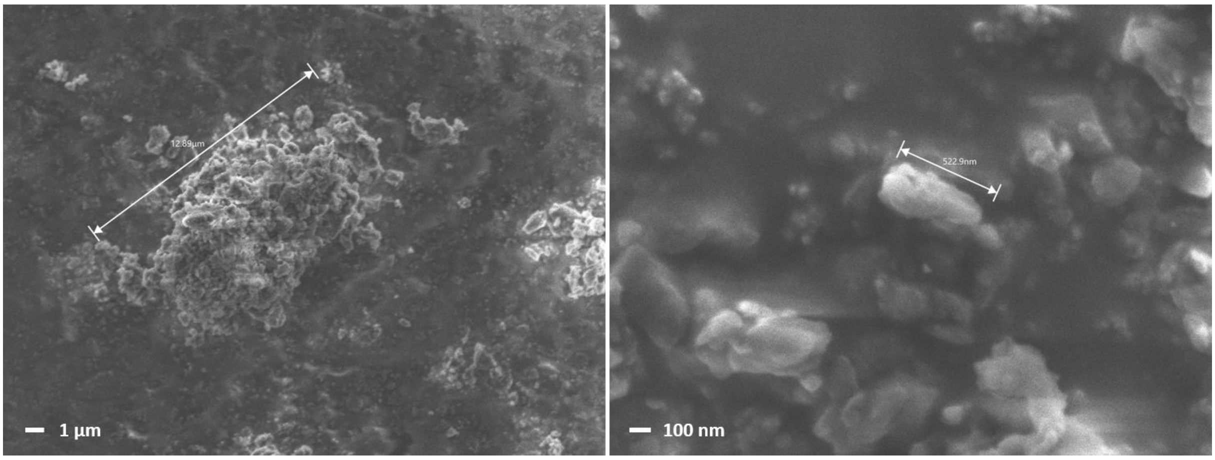


Figure S39. SEM image of the porous polymer TePE-$CHCl_3$ in a magnification of 4.5 k (left) and of 43 k (right). Smaller particles are building broader agglomerates. The measured particle sizes are 12.89 µm (left) and 522.9 nm (right).

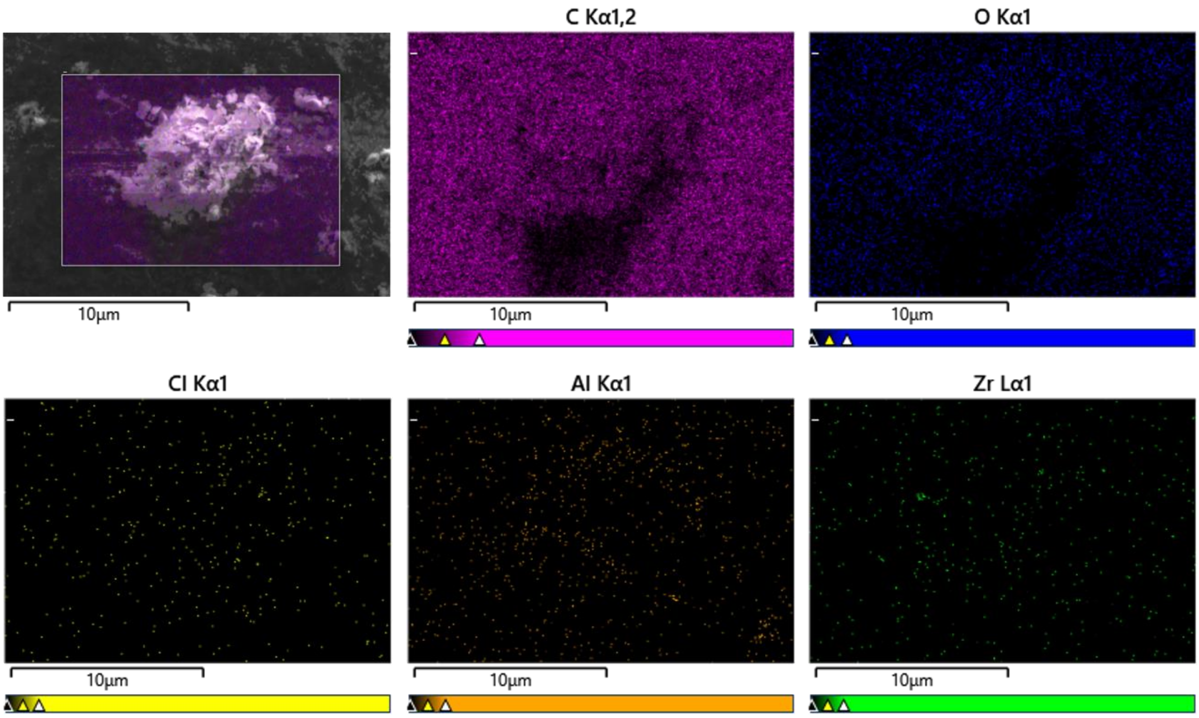


Figure S40. EDS analysis of the porous polymer TePE-$CHCl_3$ showing the amount of carbon (purple), oxygen (blue), chlorine (yellow), aluminium (orange) and zirconium (green) in a specific particle.

Table S11. EDS analysis of TePE-$CHCl_3$.

	C	O	Cl	Al	Zr
Mass %	94.18	4.75	0.71	0.36	0.00
Atom %	95.96	3.63	0.24	0.16	0.00

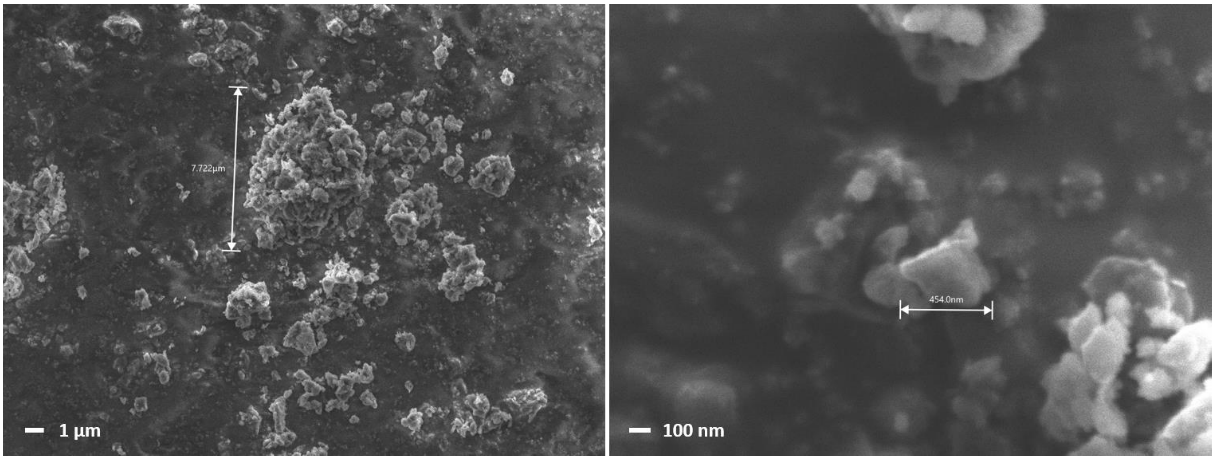


Figure S41. SEM image of the porous polymer TPB-$CHCl_3$ in a magnification of 4.5 k (left) and of 43 k (right). Smaller particles are building broader agglomerates. The measured particle sizes are 7.722 µm (left) and 454.0 nm (right).

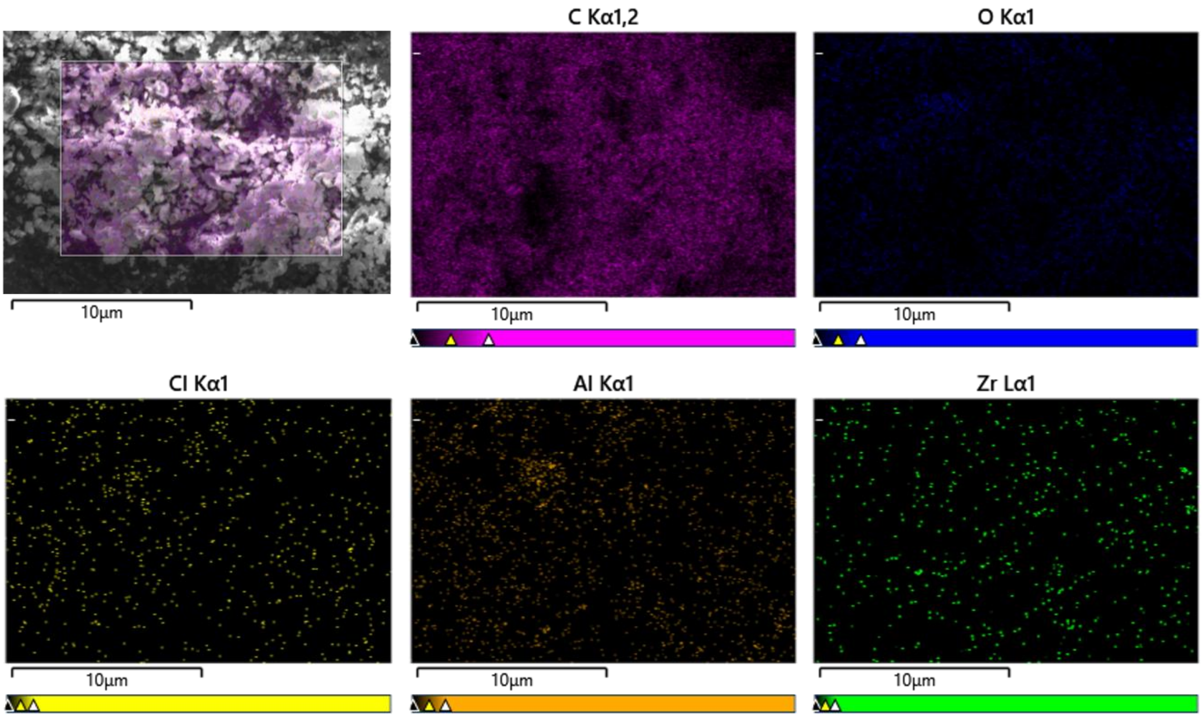


Figure S42. EDS analysis of the porous polymer TPB-$CHCl_3$ showing the amount of carbon (purple), oxygen (blue), chlorine (yellow), aluminium (orange) and zirconium (green) in a specific particle.

Table S12. EDS analysis of TPB-$CHCl_3$.

	C	O	Cl	Al	Zr
Mass %	90.47	5.98	2.01	1.54	0.00
Atom %	93.92	4.66	0.71	0.71	0.00

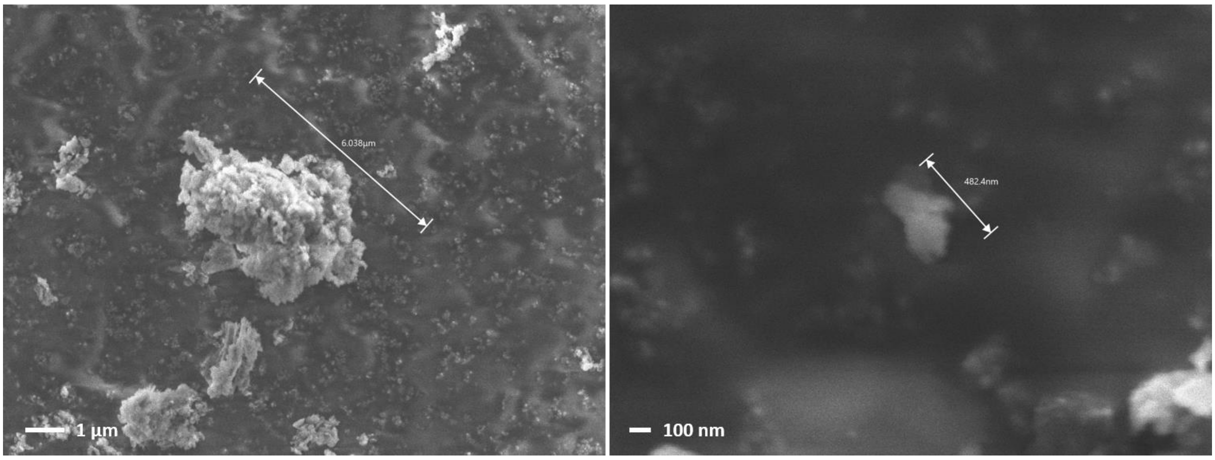


Figure S43. SEM image of the porous polymer HPB-DCM in a magnification of 8 k (left) and of 43 k (right). Smaller particles are building broader agglomerates. The measured particle sizes are 6.038 µm (left) and 482.4 nm (right).

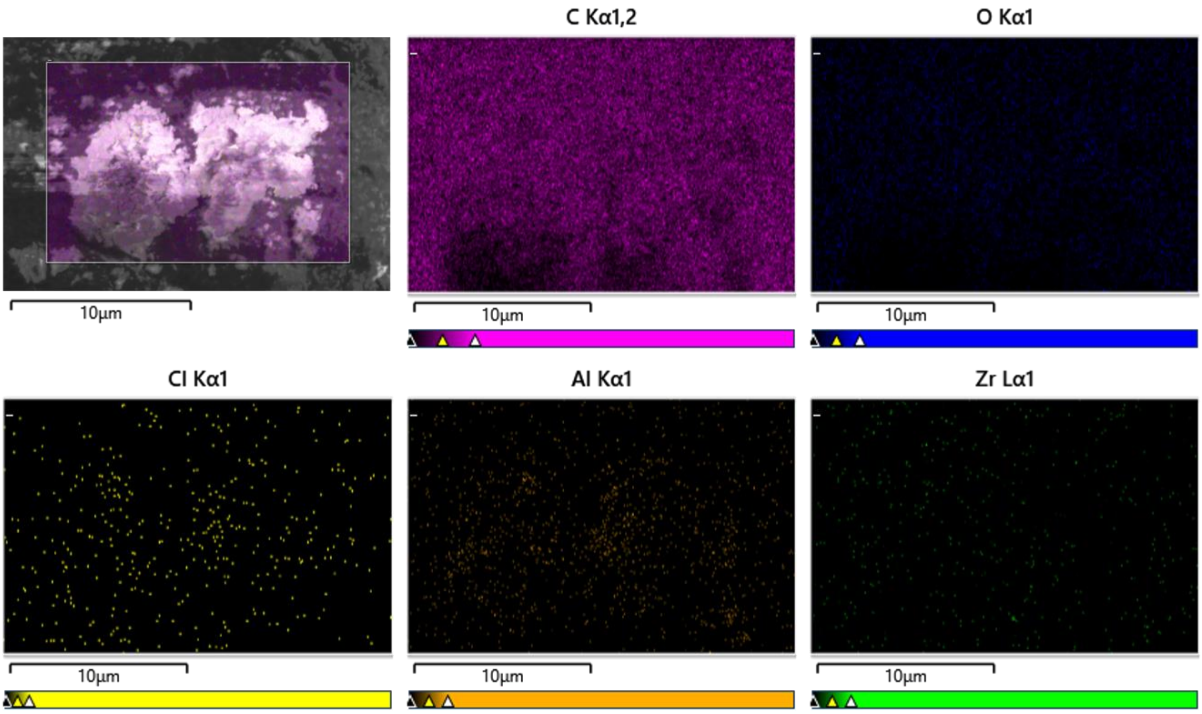


Figure S44. EDS analysis of the porous polymer HPB-DCM showing the amount of carbon (purple), oxygen (blue), chlorine (yellow), aluminium (orange) and zirconium (green) in a specific particle.

Table S13. EDS analysis of HPB-DCM.

	C	O	Cl	Al	Zr
Mass %	94.72	4.59	0.00	0.70	0.00
Atom %	96.19	3.50	0.00	0.32	0.00

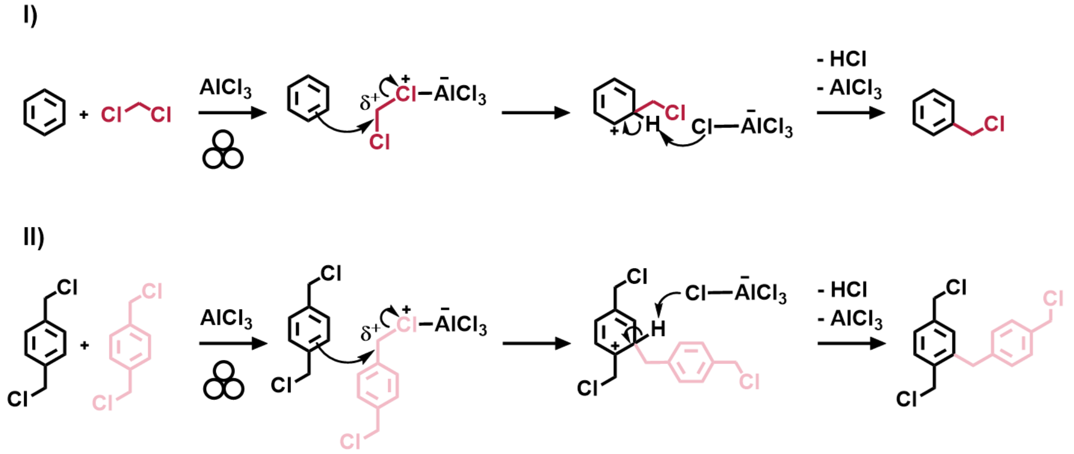


Figure S45. I) Scheme of the Friedel-Crafts reaction between a monomer and a linker, catalyzed by $AlCl_3$. The coordination of $AlCl_3$ and the linker leads to a positive polarization at the adjacent carbon that can be attacked by the high electron density of the monomer and form a polymer under release of HCl and rearomatisation. II) Scheme of the self-polymerization of a solid linker on the example of Bis(chloromethyl)benzene (BCMB). The coordination of $AlCl_3$ and the linker leads to a positive polarization at the adjacent carbon that can be attacked by the high electron density of another linker and form a polymer under release of HCl and rearomatisation.

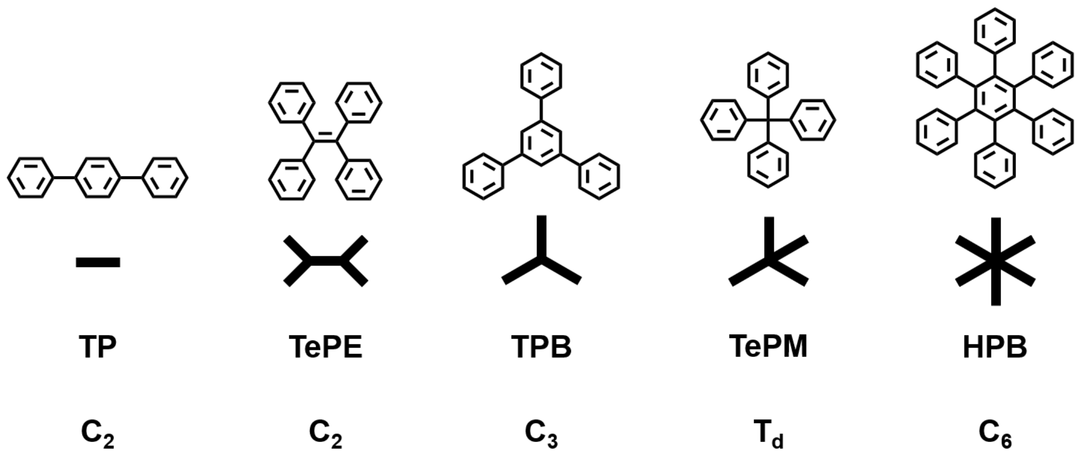


Figure S46. Schematic overview over the geometries of the C_2 monomers *p*-Terphenyl (TP) and Tetraphenylethylene (TePE), the C_3 monomer Triphenylbenzene (TPB), the T_d monomer Tetraphenylmethane (TePM) and the C_6 monomer Hexaphenylbenzene (HPB).

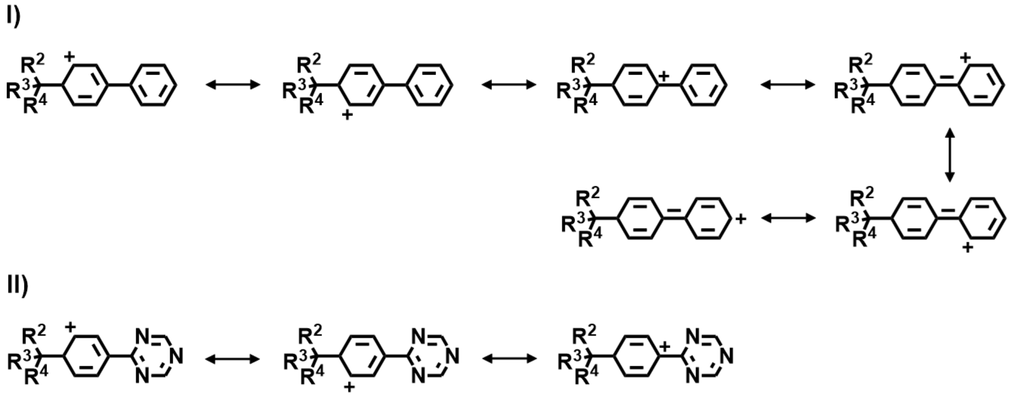


Figure S47. Resonance structures of the carbenium intermediate for the polymerization of I) the model compound Biphenyl (BP) for Triphenylbenzene (TPB) and of II) the model compound Phenyltriazine (PT) for Triphenyltriazine (TPT).