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Supporting Information

The origin of size-selective gas transport through Polymers of Intrinsic Microporosity.

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Experimental

Pure gas permeation measurements of PEEK-WC were carried out on a fixed-volume time lag instrument described in detail previously.[1] The measurements were carried out in the time lag mode on a solvent-cast membrane (from chloroform) with thickness of 67 µm and an effective area of 34.2 cm^2. All other gas permeability data were taken from the literature. Detailed physical chemical information on PEEK-WC can be found in Ref. [2].

Modelling

For the packing procedure of the polymers studied by computational methods, the general methodology used for generating realistic models of membranes is described in detail in ref. [3,4] for PEEK-WC, in ref. [5,6] for Pebax 2533, in ref. [7,8] for Hyflon AD60x and in ref. [9] for MPTB. The simulations were performed with the Materials Studio software package (Accelrys) [10]. The force field used was the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) [11], a force field suitable to explore polymer properties in general [12,13] and also those of PIMs.[9,14–16]

The accessible fractional free volume was calculated via the following equation:

$$FAV = \frac{(V_s - V_{SA})}{V_s},$$

where V_{SA} is the solvent accessible volume, which was measured with the use of the Teplyakov-Meares radii.[17]

Supplementary Figures

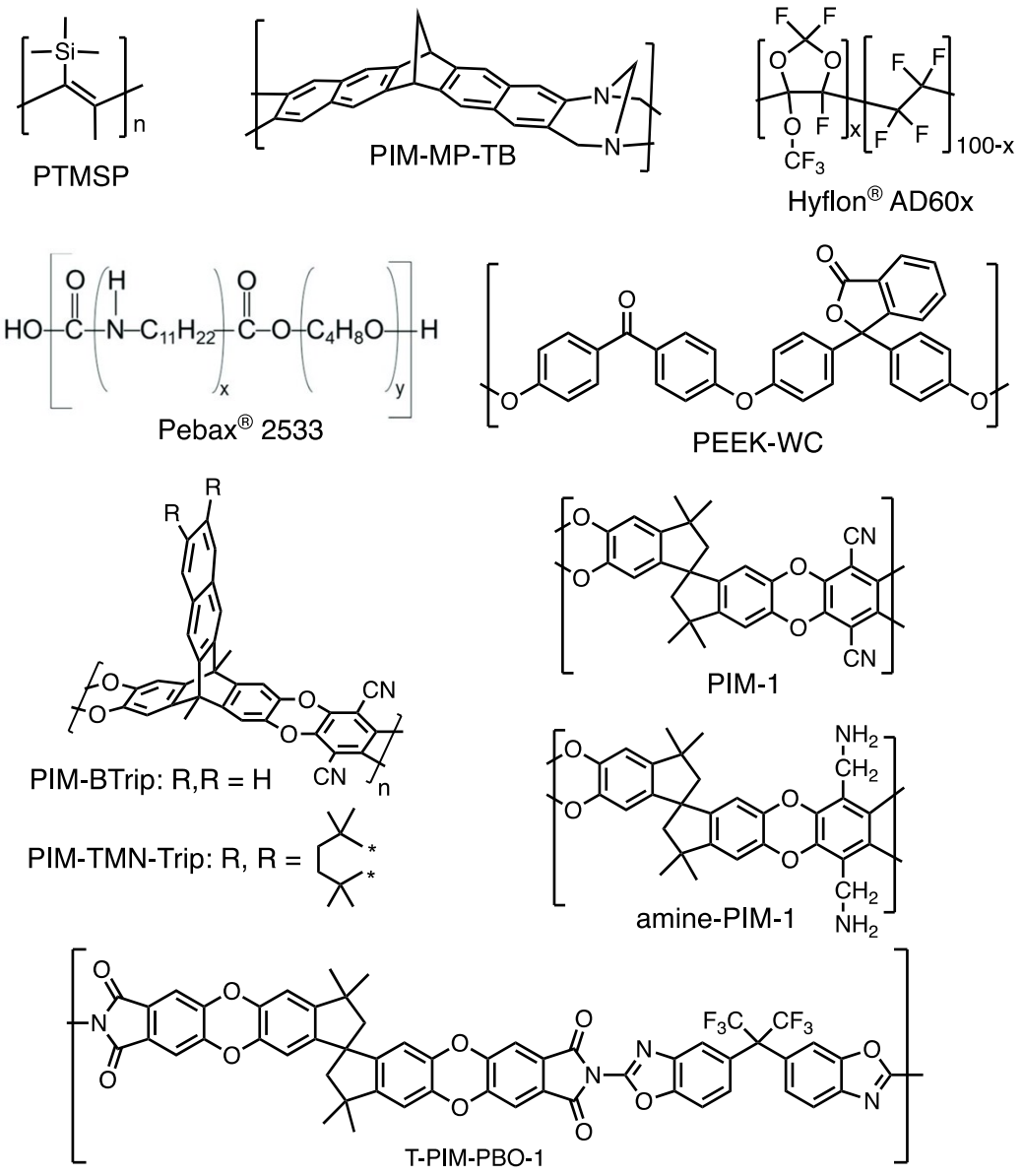


Figure SI 1. Molecular structures of the polymers discussed in the present work.

A

B

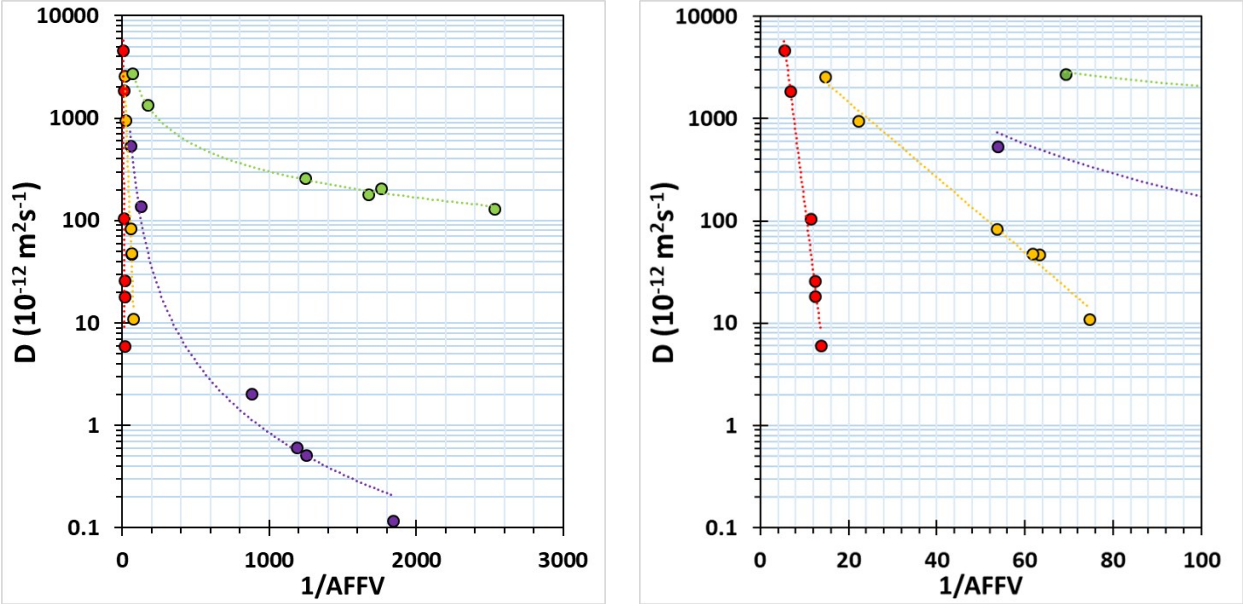


Figure SI 2. (A) Diffusion coefficient as a function of the reciprocal accessible fractional free volume (1/AFFV) for Pebax®2533[18] (green), Hyflon®AD60x[8] (orange), PEEK-WC [This work] (purple) and PIM-MP-TB[9] (red). (B) Zoom of the points corresponding to the highest AFFV.

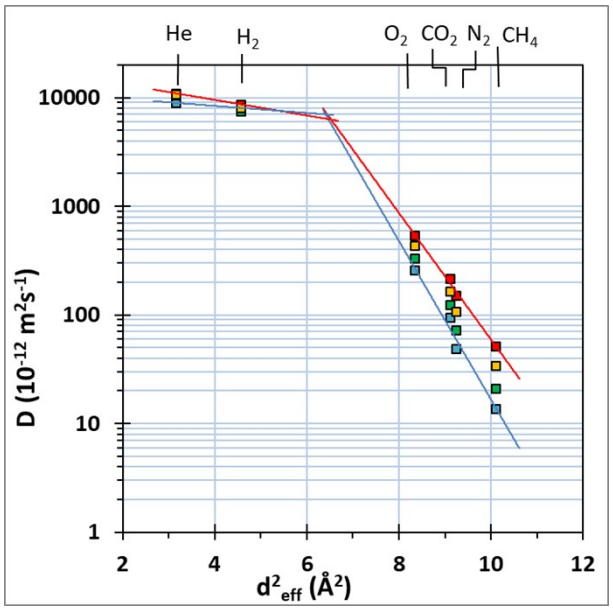
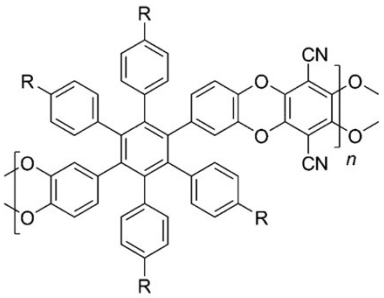
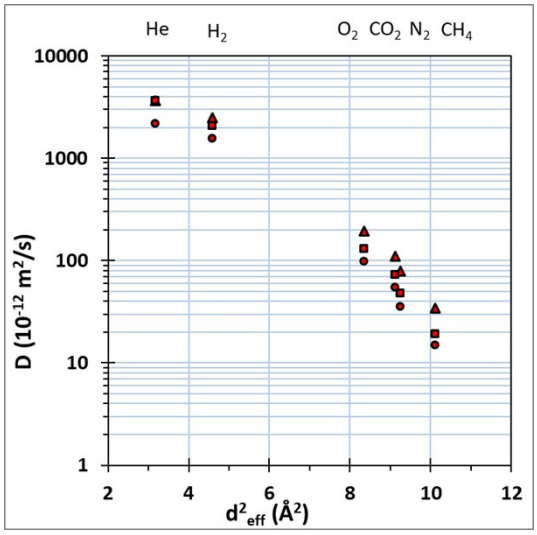


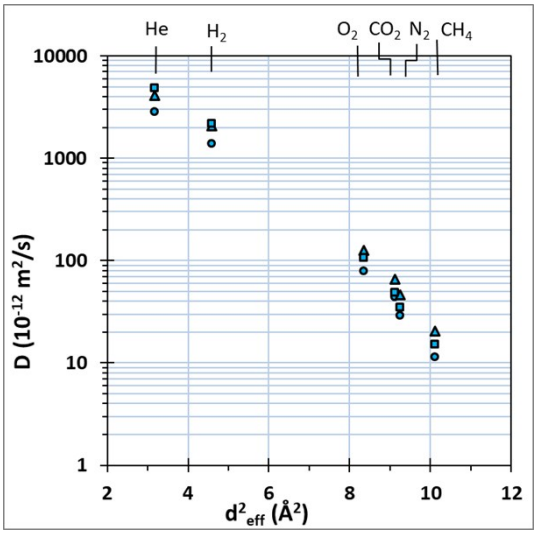
Figure SI 3. the D_a *versus* d_a^2 correlation for the PIM-BTrip after 255 days of ageing at different temperatures[19]: 25°C (blue), 35°C (green), 45°C (yellow), and 55°C (red).



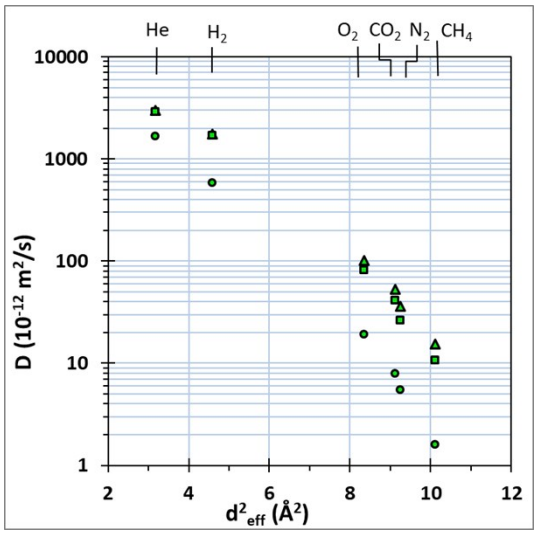
A PIM-HPB, R=H



B PIM-CH_3-HPB, R=CH_3



C PIM-Br-HPB, R=Br



D PIM-CN-HPB, R=CN

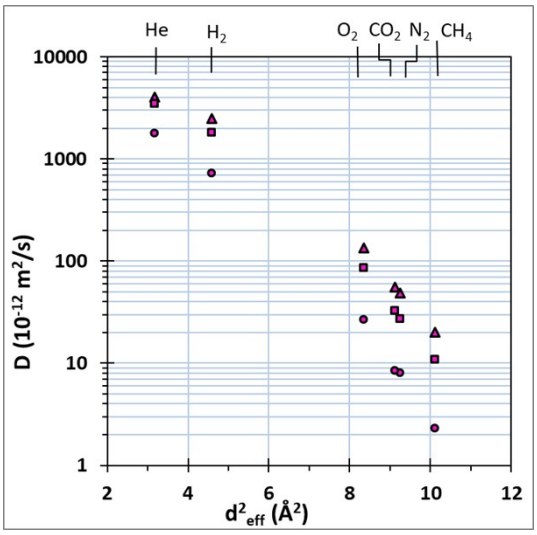


Figure SI 4. the D_a *versus* d_a^2 correlation for the Hexaphenylbenzene Based Polymers of Intrinsic Microporosity with different substitutents. Symbols: ☙ as cast sample, ❒ methanol treated sample, ❍ aged sample. Data from Carta et al.[20]

Supplementary Tables

Table SI 1. Least squares fitting parameters for determination of the best correlation using the relationship D= a e^{bx} and data from Table SI 2

		Correlation coefficient R^2 (using all 6 gases)					Correlation coefficient R^2 (using O_2, CO_2, N_2, CH_4)					T-M fitting coefficients (4gases)	
Polymer	Ref.	L-J[21]	Breck[22]	Dal-Cin[23]	Robeson [24]	T-M[17]	L-J[21]	Breck[22]	Dal-Cin[23]	Robeson [24]	T-M[17]	a	b
Pebax 1657	[18]	0.9186	0.8513	0.9067	0.8597	0.9888	0.5069	0.1195	0.5109	0.3549	0.7459	2675	-0.413
Pebax 2533	[18]	0.9014	0.8818	0.9222	0.8823	0.9970	0.3778	0.3103	0.7401	0.5942	0.9360	6677	-0.387
Hyflon AD 60x G25	[8]	0.9090	0.8781	0.9469	0.9159	0.9979	0.2173	0.5210	0.8950	0.7891	0.9949	43706	-0.690
Hyflon AD 60x G200	[8]	0.9349	0.8231	0.9871	0.9644	0.9706	0.1077	0.6226	0.9528	0.8648	0.9398	48395387	-1.639
Hyflon AD 60x H25	[8]	0.9375	0.8075	0.9843	0.9659	0.9663	0.0804	0.6736	0.9727	0.8991	0.9288	4791456	-1.259
Hyflon AD 60x H200	[8]	0.9168	0.8318	0.9783	0.9538	0.9656	0.1544	0.5544	0.9204	0.8154	0.9545	52873590	-1.628
Hyflon AD60x	[25]	0.8389	0.9284	0.9815	0.9543	0.9774	0.1264	0.5731	0.9268	0.8260	0.9308	1697363	-1.163
Hyflon AD80x	[25]	0.8012	0.9296	0.9840	0.9668	0.9545	0.1020	0.6501	0.9655	0.8857	0.9495	2682743	-1.310
Teflon AF1600	[25]	0.8442	0.9310	0.9812	0.9555	0.9818	0.1369	0.5953	0.9419	0.8475	0.9621	1024954	-0.997
Teflon AF2400	[25]	0.8741	0.9027	0.9550	0.9235	0.9893	0.2359	0.4626	0.8645	0.7410	0.9687	147254	-0.610
PIM-HPB as cast	[20]	0.8310	0.9272	0.9653	0.9470	0.9763	0.1185	0.6700	0.9497	0.8900	0.9717	904457	-1.086
PIM-HPB after MeOH	[20]	0.8408	0.9253	0.9657	0.9451	0.9804	0.1383	0.6406	0.9409	0.8718	0.9815	854658	-0.998
PIM-HPB aged 145 days	[20]	0.8392	0.9336	0.9707	0.9506	0.9836	0.1184	0.6696	0.9511	0.8905	0.9722	1337925	-1.098
PIM-CH3-HPB as cast	[20]	0.8448	0.9350	0.9709	0.9493	0.9879	0.1189	0.6679	0.9528	0.8906	0.9732	876832	-1.107
PIM-CH3-HPB after MeOH	[20]	0.8574	0.9260	0.9635	0.9397	0.9904	0.1578	0.6164	0.9222	0.8508	0.9852	735816	-1.037
PIM-CH3-HPB aged 147 days	[20]	0.8659	0.9214	0.9604	0.9350	0.9920	0.1872	0.5791	0.8971	0.8199	0.9889	1158227	-1.114
PIM-Br-HPB as cast	[20]	0.8578	0.9289	0.9716	0.9467	0.9896	0.1632	0.6034	0.9295	0.8482	0.9906	2782934	-1.417
PIM-Br-HPB after MeOH	[20]	0.8497	0.9253	0.9646	0.9425	0.9852	0.1510	0.6253	0.9276	0.8578	0.9836	934032	-1.089
PIM-Br-HPB aged 146 days	[20]	0.8441	0.9276	0.9652	0.9446	0.9833	0.1371	0.6453	0.9315	0.8691	0.9763	1518362	-1.172
PIM-CN-HPB as cast	[20]	0.8823	0.9050	0.9601	0.9296	0.9886	0.2806	0.4586	0.8454	0.7322	0.9974	2823346	-1.387
PIM-CN-HPB after MeOH	[20]	0.8748	0.9024	0.9514	0.9234	0.9866	0.2627	0.4857	0.8536	0.7508	0.9985	1042969	-1.076
PIM-CN-HPB aged 147 days	[20]	0.8776	0.9058	0.9541	0.9260	0.9886	0.2633	0.4871	0.8474	0.7484	0.9959	1427008	-1.169
PIM-BTrip-TB after MeOH	[26]	0.8608	0.8919	0.9458	0.9224	0.9676	0.2719	0.4764	0.8128	0.7246	0.9774	46730264	-1.429
PIM-BTrip-TB aged 166 days	[26]	0.8654	0.8915	0.9514	0.9256	0.9696	0.2861	0.4616	0.8300	0.7262	0.9942	73211778	-1.570
PIM-PI-EA after MeOH	[27]	0.8510	0.9017	0.9669	0.9422	0.9640	0.2399	0.5035	0.8775	0.7718	0.9993	26529132	-1.374
PIM-PI-EAaged 273 days	[27]	0.8397	0.9153	0.9693	0.9487	0.9673	0.1865	0.5770	0.9090	0.8251	0.9944	114583386	-1.624
PIM-Trip-TB after MeOH	[28]	0.8977	0.8565	0.9289	0.8949	0.9673	0.4559	0.2895	0.6900	0.5597	0.9482	13916271	-1.253
PIM-Trip-TB aged 100 days	[28]	0.8660	0.8941	0.9551	0.9291	0.9702	0.2836	0.4639	0.8335	0.7293	0.9952	183206312	-1.689

Table SI 1. Least squares fitting parameters for determination of the best correlation using the relationship D= a e^{bx} and data from Table SI 2

		Correlation coefficient R^2 (using all 6 gases)					Correlation coefficient R^2 (using O_2, CO_2, N_2, CH_4)					T-M fitting coefficients (4gases)	
Polymer	Ref.	L-J[21]	Breck[22]	Dal-Cin[23]	Robeson [24]	T-M[17]	L-J[21]	Breck[22]	Dal-Cin[23]	Robeson [24]	T-M[17]	a	b
PIM-EA-TB after MeOH	[28]	0.8948	0.8686	0.9315	0.8994	0.9747	0.4193	0.3263	0.7110	0.5918	0.9568	10931324	-1.274
PIM-EA-TB aged 470 days	[28]	0.8551	0.9176	0.9640	0.9410	0.9810	0.1924	0.5720	0.8979	0.8169	0.9921	43418981	-1.550
PIM_EA_TB as cast 70kDa	[29 30]	0.8830	0.8922	0.9487	0.9190	0.9825	0.3196	0.4242	0.8065	0.6945	0.9909	5291200	-1.284
PIM_EA_TB as cast 190kDa	[29]	0.8969	0.8812	0.9407	0.9071	0.9854	0.3860	0.3518	0.7559	0.6288	0.9751	522144	-1.080
PIM_EA_TB MeOH 70kDa	[29]	0.8951	0.8707	0.9347	0.9015	0.9773	0.4122	0.3289	0.7309	0.6032	0.9662	7525180	-1.220
PIM_EA_TB MeOH 190kDa	[29]	0.8777	0.8717	0.9394	0.9100	0.9650	0.3643	0.3778	0.7697	0.6505	0.9807	12153965	-1.279
PIM_EA_TB Modelling in MD	[29]	0.9543	0.7685	0.8692	0.8154	0.9459	0.7774	0.0296	0.3307	0.1978	0.6566	185516531	-1.729
PIM-SBI-TB	[30]	0.8863	0.8840	0.9401	0.9091	0.9825	0.3476	0.3930	0.7866	0.6673	0.9859	1144212	-1.043
PIM-SBI-TB (thinner film)	[30]	0.8702	0.8964	0.9609	0.9314	0.9758	0.2754	0.4480	0.8485	0.7272	0.9895	9143371	-1.290
1 (PTMSP)	[31]	0.7885	0.9291	0.9039	0.8902	0.9707	0.0660	0.8204	0.5427	0.6750	0.3446	12089	-0.201
2 (t-Bu)	[31]	0.8092	0.9463	0.9507	0.9371	0.9833	0.0080	0.8691	0.9121	0.9467	0.7881	47804	-0.575
3 (SiMe2CH2SiMe3)	[31]	0.8666	0.9030	0.9372	0.9108	0.9893	0.2087	0.5524	0.8783	0.7971	0.9895	180837	-0.860
4 (SiMe2CH2Ch2SiMe3)	[31]	0.8120	0.9450	0.9562	0.9427	0.9815	0.0240	0.8276	0.9262	0.9406	0.8400	89193	-0.743
5 (phenyl SiMe3)	[31]	0.8306	0.9373	0.9511	0.9350	0.9847	0.0561	0.7327	0.8552	0.8604	0.8415	62207	-0.774
6 (phenyl CF3)	[31]	0.8499	0.9400	0.9718	0.9501	0.9890	0.1236	0.6627	0.9155	0.8680	0.9559	1854936	-1.285
7 (n-C7H15)	[31]	0.6247	0.8504	0.8203	0.8402	0.8198	0.0019	0.6259	0.4646	0.5588	0.3869	7553	-0.386
8 (n-C8H17)	[31]	0.8762	0.7844	0.8872	0.8533	0.8817	0.5143	0.2241	0.5574	0.4527	0.8561	5971525	-1.104
9 (n-C6H13)	[31]	0.9024	0.8866	0.9229	0.8867	0.9986	0.3895	0.3550	0.7383	0.6219	0.9680	11351	-0.473
10 (n-C4H9)	[31]	0.8815	0.9163	0.9521	0.9209	0.9981	0.2214	0.5357	0.8801	0.7899	0.9966	47927	-0.718
11 (SiMe2-n-C6H13)	[31]	0.8795	0.8945	0.9382	0.9013	0.9938	0.2108	0.3895	0.7960	0.6603	0.8686	16728	-0.608
12 (CH(nC5H11)SiMe3)	[31]	0.9064	0.8874	0.9281	0.8931	0.9969	0.3997	0.3402	0.6967	0.5918	0.9405	27845	-0.676
13 (CH(n-C3H7)SiMe2-n-C6H13)	[31]	0.7954	0.8232	0.8593	0.8388	0.9169	0.2101	0.5367	0.9002	0.8001	0.9974	21539	-0.592
14 (Me)	[31]	0.8273	0.8918	0.9126	0.8906	0.9721	0.0758	0.7262	0.9828	0.9316	0.9463	3734	-0.668
15 (et)	[31]	0.6953	0.9551	0.9781	0.9827	0.9097	0.0052	0.8773	0.9922	0.9948	0.8175	3994614	-1.357
16 (n-C6H13)	[31]	0.6294	0.8961	0.8583	0.8810	0.8361	0.0024	0.6343	0.4699	0.5653	0.3884	41801	-0.754
17 (Cl)	[31]	0.6708	0.9266	0.9671	0.9730	0.8728	0.0226	0.8176	1.0000	0.9767	0.8723	21628797	-1.611
18 (phenyl Me)	[31]	0.9255	0.8648	0.9218	0.8788	0.9942	0.5430	0.1963	0.6068	0.4598	0.8904	32553	-0.925
19 (CH(n-C3H7)SiMe2Ph)	[31]	0.8875	0.9086	0.9482	0.9170	0.9980	0.2659	0.4850	0.8408	0.7439	0.9932	28501	-0.826
PIM-TMN-Trip (1)	[32]	0.8990	0.8557	0.9108	0.8760	0.9784	0.4853	0.2638	0.6620	0.5304	0.9342	389660	-0.708
PIM-TMN-Trip (2)	[32]	0.8750	0.8779	0.9352	0.9079	0.9698	0.3387	0.4060	0.7704	0.6660	0.9748	3546884	-1.000
PIM-TMN-Trip (3)	[32]	0.8441	0.8941	0.9497	0.9282	0.9606	0.2330	0.5227	0.8682	0.7772	0.9953	14342642	-1.165
PIM-TMN-Trip (4)	[32]	0.8408	0.9039	0.9568	0.9367	0.9629	0.2078	0.5535	0.8808	0.7989	0.9905	45794770	-1.390

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PIM-TMN-Trip (5)	[32]	0.8974	0.8574	0.9176	0.8848	0.9728	0.4632	0.2853	0.6637	0.5440	0.9331	1389698	-0.847
PIM-TMN-SBI (7)	[32]	0.8790	0.8708	0.9249	0.8953	0.9736	0.3651	0.3786	0.7646	0.6483	0.9784	554352	-0.814
PIM-TMN-SBI (8)	[32]	0.8611	0.9068	0.9493	0.9240	0.9847	0.2066	0.5513	0.8959	0.8057	0.9975	695651	-1.010
MPTB MeOH	[9]	0.8664	0.8969	0.9531	0.9285	0.9711	0.2772	0.4713	0.8136	0.7225	0.9804	55912277	-1.593
MPTB 140°C4h	[9]	0.8545	0.9112	0.9597	0.9377	0.9750	0.2127	0.5469	0.8658	0.7877	0.9838	48612441	-1.630
PIM-SBF 1	[33]	0.8323	0.9056	0.9605	0.9417	0.9575	0.1953	0.5685	0.8945	0.8134	0.9918	69556450	-1.497
2088 days aged	[33]	0.8460	0.9116	0.9637	0.9426	0.9696	0.2017	0.5607	0.8893	0.8069	0.9923	93736718	-1.666
PIM-SBF 2	[33]	0.8717	0.8902	0.9527	0.9255	0.9708	0.3059	0.4400	0.8142	0.7068	0.9916	10029069	-1.130
1295 days aged	[33]	0.8497	0.9094	0.9659	0.9433	0.9694	0.2166	0.5401	0.8873	0.7957	0.9979	281556754	-1.701
PIM-SBF 3	[33]	0.8379	0.8927	0.9537	0.9328	0.9533	0.2330	0.5214	0.8733	0.7792	0.9978	29160706	-1.354
1294 days aged	[33]	0.8374	0.9137	0.9684	0.9484	0.9643	0.1890	0.5751	0.9046	0.8219	0.9937	126805381	-1.607
PIM-SBF 4	[33]	0.8340	0.9017	0.9615	0.9416	0.9548	0.2112	0.5474	0.8895	0.8005	0.9967	93273152	-1.483
1428 days aged	[33]	0.8352	0.9117	0.9672	0.9475	0.9620	0.1896	0.5740	0.9050	0.8216	0.9941	100478043	-1.567
PIM-SBF 5	[33]	0.8819	0.8959	0.9451	0.9176	0.9832	0.3039	0.4385	0.7769	0.6861	0.9655	1221677	-0.908
1439 days aged	[33]	0.8613	0.9056	0.9588	0.9345	0.9758	0.2410	0.5136	0.8605	0.7686	0.9944	6020997	-1.150
PIM-BTrip	[34]	0.8234	0.9149	0.9627	0.9464	0.9590	0.1572	0.6182	0.9119	0.8462	0.9790	55877179	-1.411
130 days aged	[34]	0.8217	0.9132	0.9650	0.9485	0.9557	0.1640	0.6087	0.9158	0.8438	0.9856	198867660	-1.588
253 days aged	[34]	0.8114	0.9148	0.9620	0.9476	0.9528	0.1390	0.6427	0.9289	0.8665	0.9762	338131368	-1.683
365 days aged	[34]	0.8202	0.9209	0.9687	0.9528	0.9598	0.1445	0.6351	0.9265	0.8617	0.9788	344427314	-1.709
490 days aged	[34]	0.8243	0.9223	0.9692	0.9529	0.9626	0.1477	0.6310	0.9196	0.8562	0.9771	422374208	-1.762
633 days aged	[34]	0.8144	0.9248	0.9713	0.9571	0.9571	0.1340	0.6499	0.9258	0.8681	0.9708	1746108754	-1.956
PIM-Btrip (64um)	[34]	0.9121	0.8523	0.9186	0.8809	0.9781	0.5229	0.2281	0.6300	0.4923	0.9148	1063580	-0.785
120 days aged	[34]	0.8097	0.8755	0.9298	0.9133	0.9338	0.2006	0.5614	0.8940	0.8097	0.9941	37458554	-1.259
253 days aged	[34]	0.8344	0.9075	0.9592	0.9404	0.9612	0.1896	0.5761	0.8944	0.8170	0.9887	39762753	-1.288
371 days aged	[34]	0.8314	0.9090	0.9598	0.9417	0.9600	0.1824	0.5853	0.8965	0.8225	0.9858	55395141	-1.342
PIM-TMN-Trip	[34]	0.8300	0.9188	0.9659	0.9486	0.9645	0.1602	0.6142	0.9085	0.8424	0.9790	75374610	-1.393
120 days aged	[34]	0.8960	0.8553	0.9218	0.8887	0.9686	0.4601	0.2880	0.6794	0.5536	0.9431	1758234	-0.872
253 days aged	[34]	0.8556	0.8971	0.9551	0.9311	0.9677	0.2514	0.4997	0.8598	0.7613	0.9980	14042864	-1.151
358 days aged	[34]	0.8318	0.9054	0.9603	0.9415	0.9574	0.1942	0.5696	0.8972	0.8153	0.9927	58232907	-1.359
426 days aged	[34]	0.8192	0.9116	0.9609	0.9452	0.9545	0.1590	0.6158	0.9127	0.8454	0.9807	76454789	-1.408
PIM-HMI-Trip	[34]	0.8218	0.9097	0.9627	0.9461	0.9534	0.1722	0.5982	0.9085	0.8350	0.9866	145962713	-1.487
120 days aged	[34]	0.8964	0.8634	0.9231	0.8887	0.9789	0.4398	0.2987	0.7087	0.5743	0.9546	938050	-0.814

Table SI 1. Least squares fitting parameters for determination of the best correlation using the relationship D= a e^{bx} and data from Table SI 2

		Correlation coefficient R^2 (using all 6 gases)					Correlation coefficient R^2 (using O_2, CO_2, N_2, CH_4)					T-M fitting coefficients (4gases)	
Polymer	Ref.	L-J[21]	Breck[22]	Dal-Cin[23]	Robeson [24]	T-M[17]	L-J[21]	Breck[22]	Dal-Cin[23]	Robeson [24]	T-M[17]	a	b
253 days aged	[34]	0.8274	0.9075	0.9623	0.9440	0.9564	0.1826	0.5831	0.9092	0.8281	0.9927	86311289	-1.400
367 days aged	[34]	0.8336	0.9166	0.9722	0.9529	0.9622	0.1818	0.5839	0.9100	0.8290	0.9926	126330170	-1.469
426 days aged	[34]	0.8305	0.9156	0.9678	0.9497	0.9616	0.1735	0.5961	0.9102	0.8349	0.9883	143102845	-1.496
PIM-TFM-BTrip	[34]	0.8221	0.9223	0.9701	0.9541	0.9610	0.1462	0.6329	0.9233	0.8590	0.9782	184061434	-1.537
123 days aged	[34]	0.8560	0.8823	0.9451	0.9209	0.9582	0.2903	0.4576	0.8237	0.7209	0.9922	8409296	-1.077
255 days aged	[34]	0.8546	0.8993	0.9625	0.9373	0.9670	0.2461	0.4959	0.8729	0.7656	0.9991	16431316	-1.179
367 days aged	[34]	0.8278	0.9118	0.9686	0.9497	0.9578	0.1784	0.5851	0.9178	0.8335	0.9939	68058933	-1.375
496 days aged	[34]	0.8155	0.9028	0.9595	0.9429	0.9466	0.1750	0.5915	0.9172	0.8363	0.9923	145175740	-1.497
PIM-DTFM-BTrip	[34]	0.8190	0.9054	0.9620	0.9449	0.9495	0.1769	0.5896	0.9149	0.8342	0.9923	216506910	-1.557
119 days aged	[34]	0.7966	0.9033	0.9615	0.9487	0.9320	0.1592	0.6146	0.9212	0.8494	0.9855	960857142	-1.800
366 days aged	[34]	0.8108	0.9135	0.9632	0.9496	0.9478	0.1520	0.6246	0.9069	0.8463	0.9723	298390053	-1.713
490 days aged	[34]	0.7952	0.8914	0.9431	0.9309	0.9301	0.1594	0.6152	0.9088	0.8430	0.9786	438104322	-1.738
636 days aged	[34]	0.7985	0.8811	0.9344	0.9206	0.9284	0.1773	0.5918	0.9026	0.8288	0.9863	658267233	-1.857
PIM-DM-BTrip	[34]	0.8397	0.9015	0.9569	0.9361	0.9615	0.2105	0.5484	0.8896	0.8010	0.9965	23803032	-1.267
75 days aged	[34]	0.8212	0.9145	0.9641	0.9481	0.9564	0.1591	0.6157	0.9128	0.8455	0.9808	183258974	-1.574

Table SI 2. Gas diffusion coefficients used for the evaluation of R^2 values in Table SI 1

		Diffusion D_a [10^{-12} m^2s^{-1}]					
Polymer	Ref.	N_2	O_2	CO_2	CH_4	H_2	He
Pebax 1657	[18]	74	85	51	40	484	1005
Pebax 2533	[18]	205	262	180	131	1361	2740
Hyflon AD60x	[25]	47	84	48	11	954	2600
Hyflon AD80x	[25]	17	39	22	4	438	680
Hyflon AD 60x G25	[8]	78	133	82	40	1490	2910
Hyflon AD 60x G200	[8]	17	42	20	2	1010	3080
Hyflon AD 60x H25	[8]	49	103	65	12	1500	2630
Hyflon AD 60x H200	[8]	21	53	21	3	1270	2630
Teflon AF1600	[25]	116	217	129	38	1840	4020
Teflon AF2400	[25]	591	863	556	294	4980	7280
PIM-HPB as cast	[20]	35.7	97.6	54.8	14.8	1560	2160
PIM-HPB after MeOH	[20]	78.6	195	110	34.3	2490	3630
PIM-HPB aged 145 days	[20]	47.5	130	72.7	19.3	2070	3630
PIM-CH3-HPB as cast	[20]	29	78.7	43.9	11.5	1390	2840
PIM-CH3-HPB after MeOH	[20]	46.2	125	65.3	20.5	2080	4090
PIM-CH3-HPB aged 147 days	[20]	34.8	106	48.9	15.1	2183	4800
PIM-Br-HPB as cast	[20]	5.5	19	7.9	1.6	580	1660
PIM-Br-HPB after MeOH	[20]	36.2	102	52.5	15.3	1740	2970
PIM-Br-HPB aged 146 days	[20]	26.2	82.2	41.4	10.7	1700	2900
PIM-CN-HPB as cast	[20]	8	26.7	8.4	2.3	719	1790
PIM-CN-HPB after MeOH	[20]	48.7	134	55.6	20.1	2480	4040
PIM-CN-HPB aged 147 days	[20]	27.1	85.6	32.5	10.9	1820	3480
PIM-BTrip-TB after MeOH	[26]	70	347	99	28	8490	10800
PIM-BTrip-TB aged 166 days	[26]	34	160	41	10	4780	6720
PIM-PI-EA after MeOH	[27]	84	270	95	24	3360	5070
PIM-PI-EA aged 273 days	[27]	32	144	48	8.4	3581	5740
PIM-Trip-TB after MeOH	[28]	135	462	111	48.9	7800	10000
PIM-Trip-TB aged 100 days	[28]	28.5	148	34.6	7.5	4900	7700
PIM-EA-TB after MeOH	[28]	80	310	76.4	31.9	7200	10000
PIM-EA-TB aged 470 days	[28]	22.9	104	35.2	6.9	4000	7700
PIM_EA_TB as cast 70kDa	[29 30]	36.2	125.5	38.6	12.9	2986	5028
PIM_EA_TB as cast 190kDa	[29]	25.3	68.2	22.8	9.94	1200	2000
PIM_EA_TB MeOH 70kDa	[29]	99.5	318	87	36	7000	10000
PIM_EA_TB MeOH 190kDa	[29]	89	310	87	32	5000	6000
PIM_EA_TB Modelling in MD	[29]	42	150	7	6	9790	19700
PIM-SBI-TB	[30]	75	201	74	32	3500	5000
PIM-SBI-TB (thinner film)	[30]	70	187	66	19	3000	5000
1 (PTMSP)	[31]	1500	2200	2500	1600	11000	18000
2 (t-Bu)	[31]	190	370	340	140	3400	5200
3 (SiMe2CH2SiMe3)	[31]	58	140	74	31	3200	4800
4 (SiMe2CH2Ch2SiMe3)	[31]	73	170	140	48	2100	3200
5 (phenyl SiMe3)	[31]	35	98	69	26	1200	2100
6 (phenyl CF3)	[31]	10	40	19	4	790	2800
7 (n-C7H15)	[31]	130	320	310	170	1100	800
8 (n-C8H17)	[31]	180	800	180	110	1600	2700
9 (n-C6H13)	[31]	140	230	140	99	1600	3200
10 (n-C4H9)	[31]	60	120	70	34	1000	2700
11 (SiMe2-n-C6H13)	[31]	78	94	63	32	1000	2200

Table SI 2. Gas diffusion coefficients used for the evaluation of R^2 values in Table SI 1

		Diffusion D_a [10^{-12} m^2s^{-1}]					
Polymer	Ref.	N_2	O_2	CO_2	CH_4	H_2	He
12 (CH(nC5H11)SiMe3)	[31]	49	110	52	33	1100	2500
13 (CH(n-C3H7)SiMe2-n-C6H13)	[31]	92	150	99	53	2800	1400
14 (Me)	[31]	8	13	10	4	450	440
15 (et)	[31]	13	34	33	3	430	490
16 (n-C6H13)	[31]	15	86	82	25	460	490
17 (Cl)	[31]	7	22	17	1	220	220
18 (phenyl Me)	[31]	8	16	5	3	330	1100
19 (CH(n-C3H7)SiMe2Ph)	[31]	13	30	15	7	370	890
PIM-TMN-Trip (1)	[32]	572	1160	500	325	13931	16092
PIM-TMN-Trip (2)	[32]	313	934	351	159	10971	12532
PIM-TMN-Trip (3)	[32]	278	882	357	114	11517	12299
PIM-TMN-Trip (4)	[32]	105	430	154	38	8131	9869
PIM-TMN-Trip (5)	[32]	526	1355	497	297	14746	16900
PIM-TMN-SBI (7)	[32]	293	666	295	157	7739	8277
PIM-TMN-SBI (8)	[32]	59	150	73	26	3060	4351
MPTB MeOH	[9]	18	106	26	6	2869	4643
MPTB 140°C4h	[9]	11	63	18	4	2347	4041
PIM-SBF 1	[33]	60	261	91	19	4960	6007
2088 days aged	[33]	17	86	26	5	2786	4387
PIM-SBF 2	[33]	279	854	308	116	8865	12191
1295 days aged	[33]	39	191	55	10	5719	9601
PIM-SBF 3	[33]	100	365	129	34	5182	5608
1294 days aged	[33]	41	186	62	11	4111	6264
PIM-SBF 4	[33]	96	393	134	29	6189	7585
1428 days aged	[33]	47	205	70	13	4158	5920
PIM-SBF 5	[33]	239	691	293	139	6712	10178
1439 days aged	[33]	133	421	169	56	5364	7853
PIM-BTrip	[34]	101	422	172	36	7663	9299
130 days aged	[34]	72	339	122	21	7313	9112
253 days aged	[34]	49	255	94	14	8041	8935
365 days aged	[34]	39	209	75	11	6185	8634
490 days aged	[34]	28	167	56	8	5520	8404
633 days aged	[34]	19	135	43	5	5320	8227
PIM-Btrip (64um)	[34]	803	1698	641	413	15908	20606
120 days aged	[34]	303	1024	418	113	18791	12818
253 days aged	[34]	234	854	346	90	12513	14878
371 days aged	[34]	194	762	302	73	12083	14416
PIM-TMN-Trip	[34]	160	667	271	59	11612	15939
120 days aged	[34]	550	1364	496	286	12470	13988
253 days aged	[34]	320	964	383	127	11490	14287
358 days aged	[34]	184	690	266	64	10214	12012
426 days aged	[34]	144	594	241	51	10120	11428
PIM-HMI-Trip	[34]	134	584	218	43	10040	11845
120 days aged	[34]	542	1134	464	264	13769	16739
253 days aged	[34]	189	710	277	61	11259	13234
367 days aged	[34]	145	579	216	44	8294	12847
426 days aged	[34]	124	531	197	39	9530	13325
PIM-TFM-BTrip	[34]	103	474	186	33	9456	13496

Table SI 2. Gas diffusion coefficients used for the evaluation of R^2 values in Table SI 1

		Diffusion D_a [10^{-12} m^2s^{-1}]					
Polymer	Ref.	N_2	O_2	CO_2	CH_4	H_2	He
123 days aged	[34]	375	1109	430	165	10325	11102
255 days aged	[34]	317	859	347	108	9084	12350
367 days aged	[34]	196	672	274	61	8922	11621
496 days aged	[34]	131	518	195	38	9033	9382
PIM-DTFM-BTrip	[34]	111	473	170	31	8914	9959
119 days aged	[34]	49	274	88	12	5227	5437
366 days aged	[34]	30	183	62	9	4160	4981
490 days aged	[34]	37	218	71	11	6872	4982
636 days aged	[34]	19	122	35	5	6311	3788
PIM-DM-BTrip	[34]	182	608	242	66	8928	10288
75 days aged	[34]	73	354	129	23	7811	9716

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